CHAPTER-4

COPPER-CATALYZED *N*-ARYLATION OF SULFOXIMINES WITH ARYLBORONIC ACID UNDER MILD CONDITION

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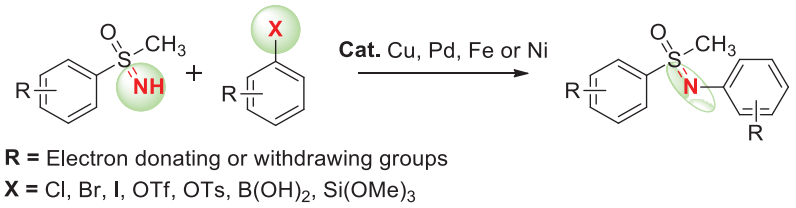
4.1 INTRODUCTION

Sulfoximines are mono-aza analogous of sulfones which received considerable interest in chemistry and biology [1, 2]. Sulfoximine motifs were found in many drugs, bioactive molecules and natural products [1-3]. It has been observed that the functionalization of sulfoximines at nitrogen center provides interesting biological and chemical properties. In this context, *N*-aryl of sulfoximines has been explored as efficient chiral ligands in asymmetric synthesis [4-8]. 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 [9].

N-Arylation of sulfoximine can be achieved using numerous aryl donors such as aryl halides [10-14], arylboronic acids [15], aryl triflates [16], aryl siloxanes [17], arynes [18] and diaryliodonium salt [19], etc., in the presence of Cu, Pd, Fe and Ni catalysts (**Scheme 4.1**). Among the different methods, Bolm's copper mediated *N*-arylation of sulfoximine with arylboronic acids (under *Chan-Lam* reaction condition) was found more impressive from synthetic perspective [15]. Because, the *N*-arylation takes place at room temperature in the presence of catalytic amount of copper acetate under mild reaction condition. Moreover, arylboronic acids are cheap, commercially available, and less toxic in nature which can be easily stored and handled.

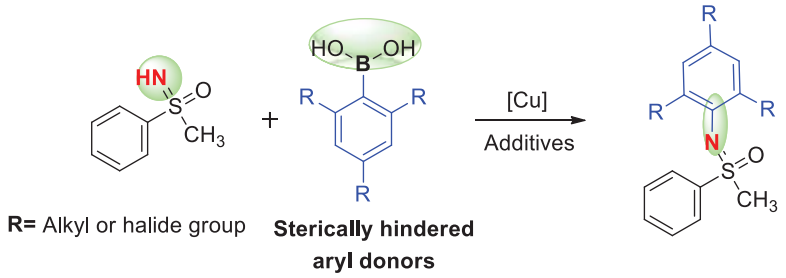


Scheme 4.1. Previous reports on *N*-arylation of sulfoximines.

Despite having many advantages, this method has some serious limitations. For example, *N*-arylation of sulfoximine with sterically hindered 2,4,6-trimethylphenylboronic acid has failed to yield the desired product. Moreover, use of excess amount of arylboronic acids (2.3 equiv.) and longer reaction time (12 h) make this protocol less attractive. The use of excess amount of boronic acid may attribute to the side reactions during the *N*-arylation such as formation of phenols (*via* oxidative hydrolysis) and biaryl compounds (*via* oxidative homo-coupling) [20]. On the other hand, unlike other secondary amines, the nitrogen of sulfoximines possesses poor nucleophilicity [2, 21] which might require different reaction conditions for the *N*-arylation with sterically hindered aryl donors.

Nevertheless, it can be noticed that most of the other reports on *N*-arylation of sulfoximine, also did not explore the *N*-arylation reaction with sterically hindered aryl donors. It clearly demonstrates that the formation *C-N* bond in sulfoximine with sterically hindered aryl donor is a difficult task. Nevertheless, we believe that such sterically hindered *N*-aryl sulfoximines might play an important role in asymmetric catalysis [4] as well as in drug discovery [9].

In view of this, our objective was to re-investigate the *N*-arylation of sulfoximine with various arylboronic acids including sterically hindered one, using copper catalysts under different reaction conditions (**Scheme 4.2**).



Scheme 4.2. Objective of the present work.

4.2 RESULTS AND DISCUSSION

4.2.1 Optimization of reaction condition

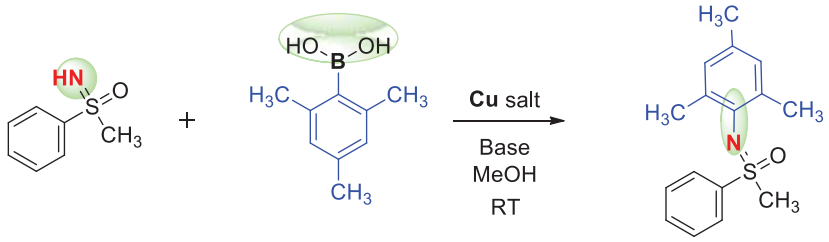
At the outset, in order to optimize the reaction condition, *N*-arylation of *S*-methyl-*S*-phenylsulfoximine (**1a**) was investigated with sterically hindered 2,4,6-trimethylphenylboronic acid (**2a**) in the presence of various copper salts in methanol (**Table 4.1**). Initially, the reaction was carried out with 1 mmol of sulfoximine and 1.2 equiv. of 2,4,6-trimethylphenylboronic acid (**2a**) in the presence of 10 mol% of $Cu(OAc)_2$ at room temperature. As reported by Bolm*et al*., no reaction was observed even after 12 h at room temperature [15]. In fact, other Cu(I) and Cu(II) salts such as $CuSO_4$, CuCl, CuBr and CuI were also failed to give the desired product in methanol (**Table 4.1**, **entries 2-5**).

It is well known that ligands and bases play an important role in cross-coupling reactions particularly if the substrates are poor reactive or sterically hindered [22-25]. In fact, in the chapter 3, we have successfully demonstrated *N*-alkylation of sulfoximines

with different alkylboronic acids in the presence of copper(II) acetate and pyridine [26]. In light of this, we were interested to perform the *N*-arylation reaction with copper(II) acetate in the presence of pyridine and 4-DMAP. The reason behind the selection of pyridine and 4-DMAP is that they can act as bases as well as ligands for copper. In fact, combination of copper with pyridine and 4-DMAP display good catalytic activity and selectivity in many organic transformations [27-34].

Hence, *N*-arylation of *S*-methyl-*S*-phenylsulfoximine (1mmol) **(1a)** with 2,4,6-trimethylphenylboronic acid (1.2 equiv.) **(2a)** was carried out in the presence of 1 equiv. of pyridine and 4-DMAP using 10 mol% of copper(II) acetate in methanol (**Table 4.1**, **entries 6** and **7**). To our delight, the reaction proceeded smoothly while *N*-(2,4,6-trimethyl)phenyl-*S*-methyl-*S*-phenylsulfoximine **(3aa)** was obtained in 59 % and 77%, respectively (**Table 4.1**, **entries 6** and **7**). Encouraged, the reaction was further investigated with various organic and inorganic bases such as DABCO, DBU, Et_3N and K_2CO_3 as well as the ligand 2,2'-bipyridine (2,2'-bipy) (**Table 4.1**, **entries 8-12**). Unfortunately, no significant yield of the desired product was obtained suggests that the reaction needs both base as well as ligand. Further, the reaction was performed with different copper slats in the presence of 4-DMAP in methanol at room temperature (**Table 4.1**, **entries 7** and **13-16**). Among all, copper iodide/4-DMAP system produces the desired product **3aa** in high yield (*i.e.* 89%) within 4 h under open air condition (**Table 4.1**, **entry 16**).

Table 4.1. Optimization of reaction condition for *N*-arylation of sulfoximine **(1a)** with 2,4,6-trimethylphenylboronic acid **(2a)**.[a,b]



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

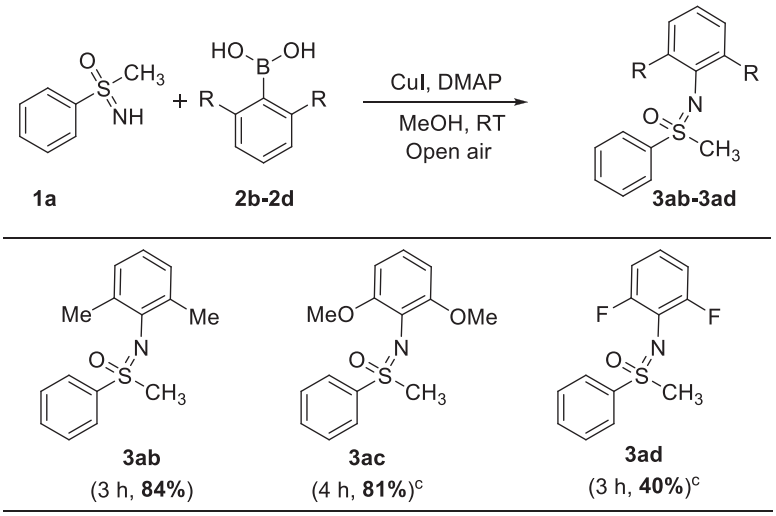
Entry	Catalyst (10 mol%)	Base (1 equiv.)	Time (h)	Yield (%)[b]
1	$Cu(OAc)_2$	-	12	n.r
2	$CuSO_4$	-	12	n.r
3	CuCl	-	12	n.r
4	CuBr	-	12	n.r
5	CuI	-	12	n.r
6	$Cu(OAc)_2$	py	12	59
7	$Cu(OAc)_2$	4-DMAP	12	77
8	$Cu(OAc)_2$	DABCO	12	n.r
9	$Cu(OAc)_2$	DBU	12	n.r
10	$Cu(OAc)_2$	Et_3N	12	~7
11	$Cu(OAc)_2$	K_2CO_3	12	n.r
12	$Cu(OAc)_2$	2,2'-bipy	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**

[a]**Reaction condition:** Sulfoximine (1.0 mmol), 2,4,6-trimethylboronic acid (1.5 equiv.), Copper salt (0.1 equiv.), base (1.0 equiv.), MeOH (2 mL) were stirred at room temperature under open air condition. [b]Isolated yield.

4.2.2 Substrates scope

Having established the optimized condition, the reaction of *N*-arylation of *S*-methyl-*S*-phenylsulfoximine (**1a**) was investigated with different sterically hindered *i.e.* 2,6-dimethyl, 2,6-dimethoxy and 2,6-difluorophenylboronic acids (**Table 4.2**, **3ab-3ad**). To our delight, *N*-arylation underwent smoothly under optimized condition within 4 hours and desired products were obtained in 40-84% yields (**Table 4.2**, **3ab-3ad**).

Table 4.2. *N*-Arylation of *S*-methyl-*S*-phenylsulfoximine **(1a)** using sterically hindered arylboronicacid.[a,b]



[a]**Reaction condition:** *S*-Methyl-*S*-phenylsulfoximine (0.967 mmol, 0.150 g), arylboronic acid (1.5 equiv.), CuI (0.1 equiv., 0.018 g), DMAP (1.0 equiv., 0.118 g), MeOH (2 mL) stirred at room temperature under open air condition. [b]Isolated yield. [c]arylboronic acid (2.4 equiv.) and CuI (0.2 equiv.) was used.

Prompted, various substituted boronic acids were subjected for the *N*-arylation with *S*-methyl-*S*-phenylsulfoximine **(1a)** under optimized condition and the result is summarized in **Table 4.3**. *N*-Arylation of *S*-methyl-*S*-phenylsulfoximine **(1a)** with phenylboronic acid (1.2 equiv.) yields the desired product *N*-phenyl *S*-methyl-*S*-phenylsulfoximine in 91% yield within 45 mins at room temperature (**Table 4.3**, **3ae**).

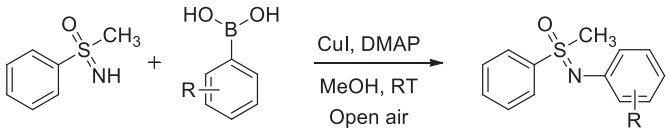
It is noteworthy that under the Bolm's reaction conditions, *N*-phenyl *S*-methyl-*S*-phenylsulfoximine was obtained in a comparable yield (*i.e.* 93%), however after 12 h in the presence of 2.3 equivalent of phenylboronic acid. This clearly demonstrates the advantage and credential of the current methodology over other methods.

Encouraged, various arylboronic acids bearing electron donating (e.g. Et, OMe and SMe) and withdrawing groups (F, Cl, Br and NO_2) at the *para*-position were subjected for the *N*-arylation with sulfoximine **1a** under optimized condition. All these reactions proceeded smoothly while the desired *N*-arylated products were obtained in good to excellent yield **(86-91%)** within 90 mins (**Table 4.3**, **3af-3al**). In fact, there was no significant difference in the yields was observed between electron donating and withdrawing groups functionalized arylboronic acids. Similar to *para*-substituted arylboronic acids, *N*-arylation of sulfoximine**1a** with *meta*-substituted arylboronic acids were achieved in good yield (**Table 4.3**, **3am** and **3an**).

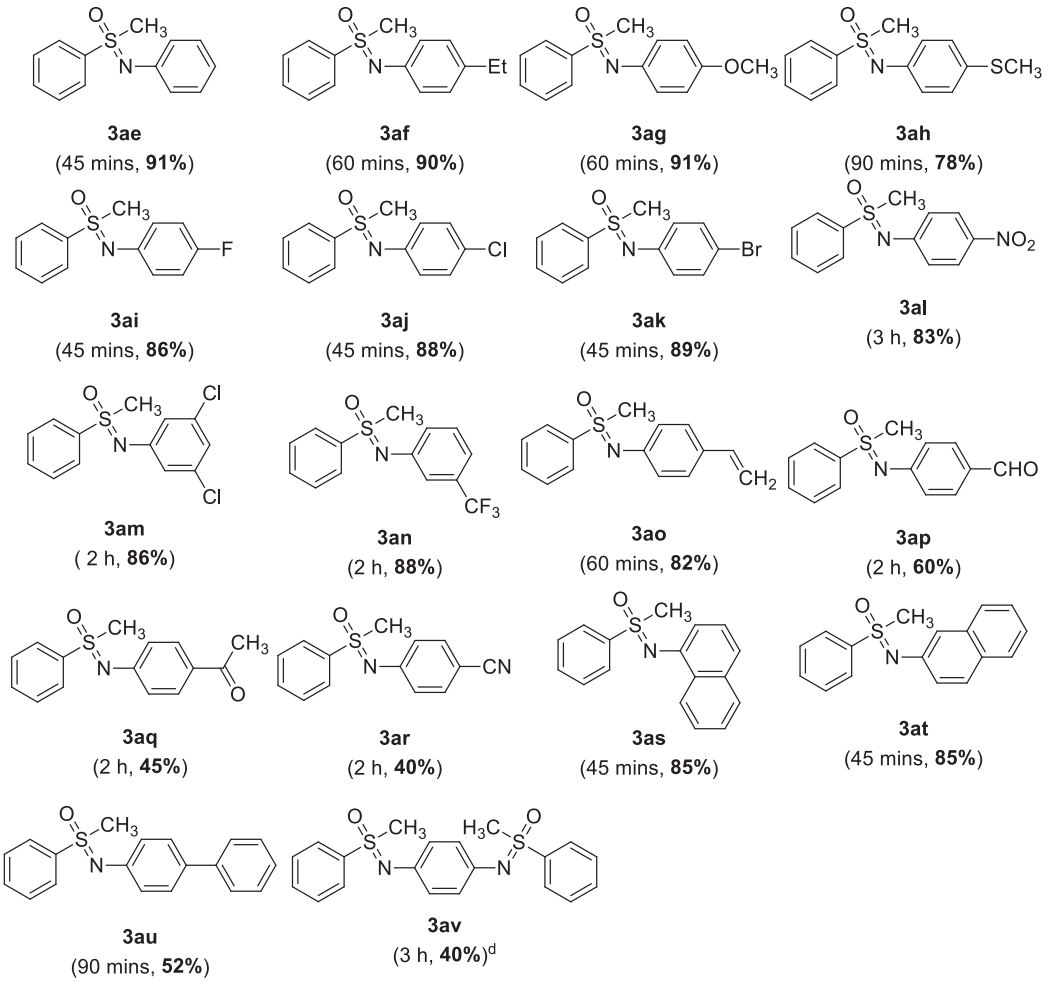
To investigate the versatility of the developed methodology, various sensitive group functionalized arylboronic acids such as 4-vinyl, formyl, acyl and cyano-phenylboronic acids were subjected for the *N*-arylation with *N*-phenyl-*S*-methyl-*S*-phenylsulfoximine. To our delight, *N*-arylation was successfully accomplished in good yield under optimized reaction condition while sensitive functional groups remained intact (**Table 4.3**, **3ao-3ar**). Likewise, more conjugated arylboronic acids such as naphthyl and biphenyl-bornic acids also showed efficiency similar to that of simple arylboronic acid and gave the desired products in good yields (**Table 4.3**, **3as-3au**).

Later, sulfoximine**1a** was subjected to the *N*-aryaltion with benzene 1,4-diboronic acid which affords bis-sulfoximine product in 40% yield(**Table 4.3**, **3av**).

Table 4.3. *N*-Arylation of *S*-methyl-*S*-phenylsulfoximine **(1a)** using various arylboronicacid.[a,b,d]



1a **2e-2v** **3ae-3av**



3ae (45 mins, **91%**)

3af (60 mins, **90%**)

3ag (60 mins, **91%**)

3ah (90 mins, **78%**)

3ai (45 mins, **86%**)

3aj (45 mins, **88%**)

3ak (45 mins, **89%**)

3al (3 h, **83%**)

3am (2 h, **86%**)

3an (2 h, **88%**)

3ao (60 mins, **82%**)

3ap (2 h, **60%**)

3aq (2 h, **45%**)

3ar (2 h, **40%**)

3as (45 mins, **85%**)

3at (45 mins, **85%**)

3au (90 mins, **52%**)

3av (3 h, **40%**)[d]

[a]**Reaction condition:** *S*-Methyl-*S*-phenylsulfoximine (0.967 mmol, 0.150 g), arylboronic acid (1.5 equiv.), CuI (0.1 equiv., 0.018 g), 4-DMAP (1.0 equiv., 0.118 g), MeOH (2 mL) was stirred at room temperature under open air condition. [b]Isolated yield. [d] Arylboronic acid (3 equiv.) was used.

Having explored the scope of different arylboronic acids, *N*-arylation of different sulfoximines were also investigated. To explore the protocol, 4-methylphenylboronic acid was taken as a common aryl donor and subjected with variety of sulfoximines under optimized condition (**Table 4.4**, **3ay-3ly**). The *S*-alkyl-*S*-phenylsulfoximines bearing linear or branched alkyl chains underwent *N*-arylation smoothly with 87-92% yield under optimized condition (**Table 4.4**, **3ay-3ey**).

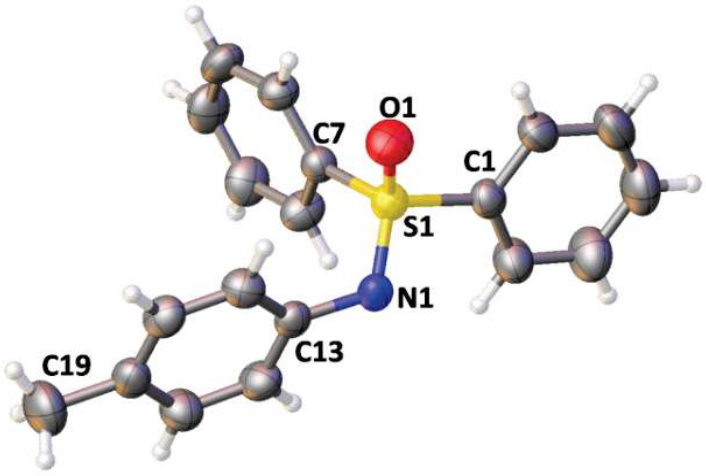
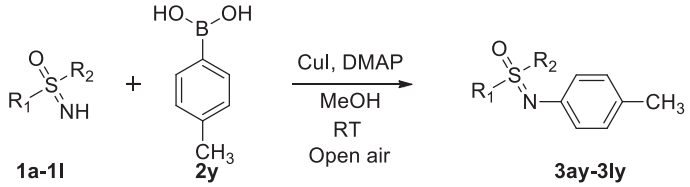


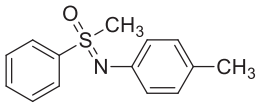
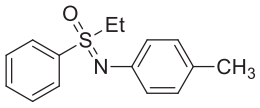
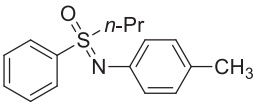
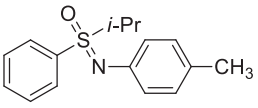
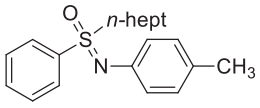
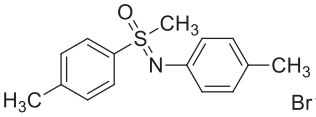
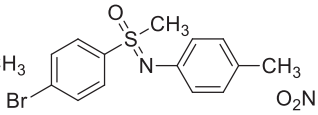
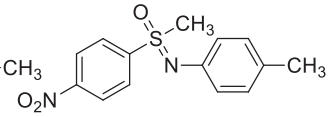
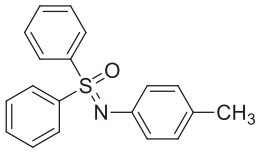
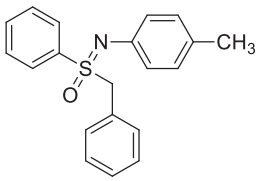
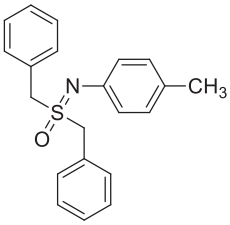
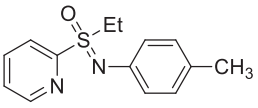
Figure 4.1 Single crystal XRD structure of compound **3iy**.

Notably, *N*-arylation takes place in good yield with the sterically hindered *S*-phenyl-*S*-*iso*-propylsulfoximine within 90 mins (**Table 4.4**, **3dy**). The substrates bearing electron donating and withdrawing groups on the sulfoximine aryl ring also underwent *N*-arylation and provide the desired products in 89-94% yields (**Table 4.4**, **3fy-3hy**). Further, *N*-arylation of *S,S*-diphenyl, *S*-benzyl-*S*-phenyl, *S,S*-dibenzylsulfoximines and *S*-ethyl-*S*-pyridylsulfoximine (*i.e.*

heteroaromaticsulfoximine) were performed under optimized reaction condition to demonstrate the versatility of the current methodology (**Table 4.4**, **3iy**-**3ly**). All these substrates were successfully *N*-arylated in 81-93% yield with 4-methylphenylboronic acid in a short span of time. To our delight, the single crystal XRD of compound **3iy** also reveals the formation of desired product (**Figure 4.1**).

Table 4.4. *N*-Arylation of various sulfoximines using 4-methylphenylboronic acid.[a,b]



 **3ay** (1 h, **91%**)	 **3by** (45 mins, **92%**)	 **3cy** (45 mins, **92%**)	 **3dy** (90 mins, **87%**)
 **3ey** (90 mins, **90%**)	 **3fy** (1 h, **89%**)	 **3gy** (45 mins, **92%**)	 **3hy** (2 h, **91%**)
 **3iy** (1 h, **84%**)	 **3jy** (1 h, **83%**)	 **3ky** (90 mins, **81%**)	 **3ly** (2 h, **93%**)

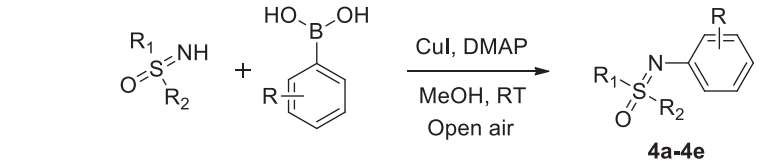
[a]**Reaction condition:** Sulfoximine (0.150 g, 1 equiv.), 4-methylphenylboronic acid (1.5 equiv.), CuI (0.1 equiv.), 4-DMAP (1.0 equiv.), MeOH (2 mL) were stirred at room temperature under open air condition. [b]Isolated yield.

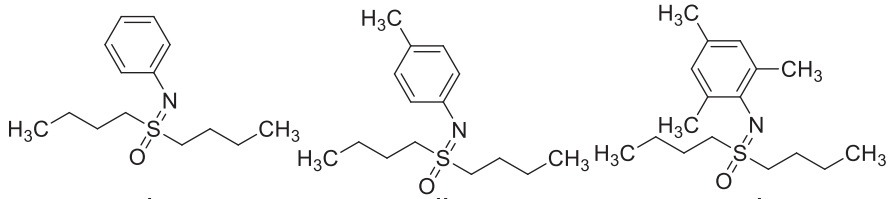
Table 4.5. Crystal data and structure refinement for **3ay**.

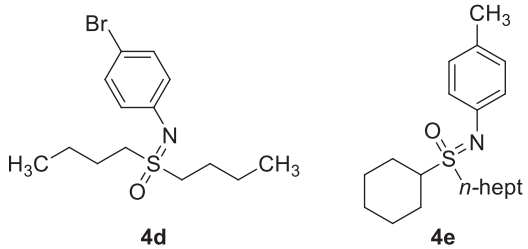
CCDC	1848196
Empirical formula	$C_{19}H_{17}NOS$
Formula weight	307.42
Temperature/K	296.15
Crystal system	Monoclinic
Space group	$P2_1/c$
a/Å	10.2355(7)
b/Å	8.0687(4)
c/Å	19.5055(12)
α/°	90
β/°	97.874(2)
γ/°	90
Volume/Å^3	1595.72(17)
Z	4
ρ_{calc}mg/mm^3	1.2795
m/mm^{-1}	0.204
F(000)	648.7
Crystal size/mm^3	0.2 × 0.15 × 0.15
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection	4.22 to 57.82°
Index ranges	$-13 \leq h \leq 13$, $-10 \leq k \leq 10$, $-26 \leq l \leq 26$
Reflections collected	21793
Independent reflections	4180 [R_{int} = 0.0408, R_{sigma} = 0.0377]
Data/restraints/parameters	4180/0/199
Goodness-of-fit on F^2	1.082
Final R indexes [I>=2σ (I)]	R_1 = 0.0543, wR_2 = 0.1488
Final R indexes [all data]	R_1 = 0.0965, wR_2 = 0.1847
Largest diff. peak/hole / e Å^{-3}	1.36/-0.35

$^{a}R_1=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, $^{b}wR_2=|\Sigma_w(|F_o|^2-|F_c|^2)|/\Sigma|w|(F_o)^2|^{1/2}$

Table 4.6. *N*-Arylation of aliphatic sulfoximines using various arylboronic acids.





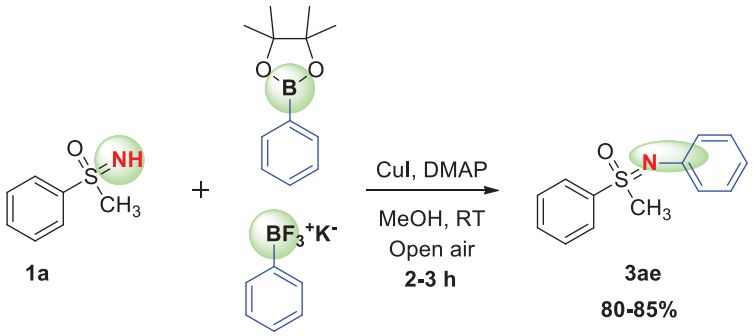


[a]**Reaction condition:** Sulfoximine (0.150 g, 1 equiv.), arylboronic acid (1.5 equiv.), CuI (0.1 equiv.), DMAP (1.0 equiv.), MeOH (2 mL) were stirred at room temperature under open air condition. [b]Isolated yield.

The *N*-arylation protocol was further extended to dialkylsulfoximines such as *S,S*-dibutylsulfoximine and *S*-cyclohexyl-*S*-heptylsulfoximine (**Table 4.6**, **4a-4e**). Initially, *S,S*-dibutylsulfoximine was subjected for the *N*-arylation with different arylboronic acids including sterically hindered one, under optimized condition (**Table 4.6**, **4a-4d**). The reactions proceeded smoothly at room temperature while the desired products were obtained in 71-92% yields (**Table 4.6**, **4a-4d**). More interestingly, the sterically hindered 2,4,6-trimethylphenylboronic acid underwent coupling reaction in

good yield with high efficiency (**Table 4.6**, **4c**). Likewise, *N*-arylation of *S*-cyclohexyl-*S*-heptylsulfoximine with 4-methylphenylboronic acid affords corresponding *N*-arylated product in good yield (83%) (**Table 4.6**, **4e**).

It is also noteworthy that the arylboronic acid surrogates such as phenylboronic acid pinacol ester and potassium trifluorophenylborate also participate in the coupling reaction very efficiently and gave *N*-arylated product **3ae** in 80% and 85% yields, respectively in 2-3 hours (**Scheme 4.3**, **3ae**).

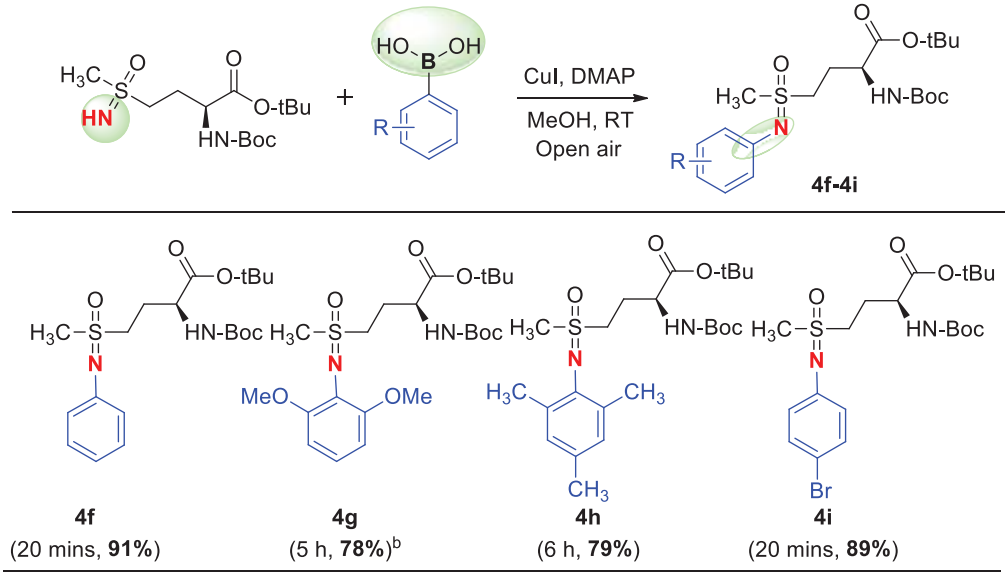


Scheme 4.3. *N*-Arylation of *S*-methyl-*S*-phenylsulfoximine using phenylboronic acid surrogates.

Methionine sulfoximine (MSO) and buthionine sulfoximine (BSO) are the naturally occurring biologically relevant sulfoximines play an important role in drug discovery [1, 35]. For instance, methionine sulfoximine (MSO) and buthionine sulfoximine (BSO) inhibit γ-glutamylcysteine synthetase and glutamine synthetase enzymes, respectively and display important therapeutic benefits for several human diseases [36, 37]. It is noteworthy that so far no method has been developed for the *N*-arylation of these bioactive sulfoximines. In this context, protected L-methionine sulfoximine derivative was synthesized and subjected for *N*-arylation with simple as

well as sterically hindered arylboronic acids (**Table 4.7**). To our delight, *N*-arylated L-methionine sulfoximines were obtained in 78-91% yield under optimized condition. In fact, *N*-arylation with sterically hindered 2,4,6-trimethylphenylboronic acid afforded corresponding *N*-arylated product **4h** in 79% yield however it requires little longer reaction time. It is worth to mention that during the *N*-arylation of protected L-methionine sulfoximine, *Boc*-protected amine was remained intact (**Table 4.7**, **4f-4i**).

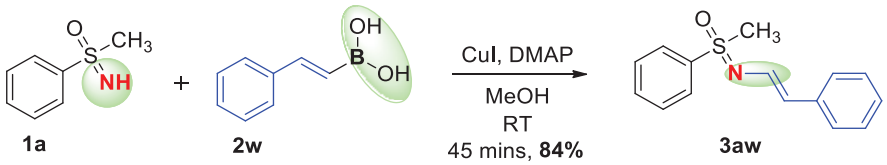
Table 4.7. *N*-Arylation of bio-active L-methionine sulfoximine with arylboronic acids.[a,b]



[a]**Reaction condition:** Protected-L-methionine sulfoximine (1 equiv., 0.150 g), arylboronic acid (1.5 equiv.), CuI (0.1 equiv., 0.018 g), DMAP (1.0 equiv., 0.118 g), MeOH (2 mL) were stirred at room temperature under open air condition. [b]Arylboronic acid (2.4 equiv.) and CuI (0.2 equiv.) was used. [b]Isolated yield.

N-Vinylsulfoximines, i.e. enamide analogues of sulfoximine, play an important role in synthetic organic chemistry as well as in biology [38-40]. Synthesis of vinylsulfoximines has been demonstrated by metal-catalyzed cross-coupling reaction of

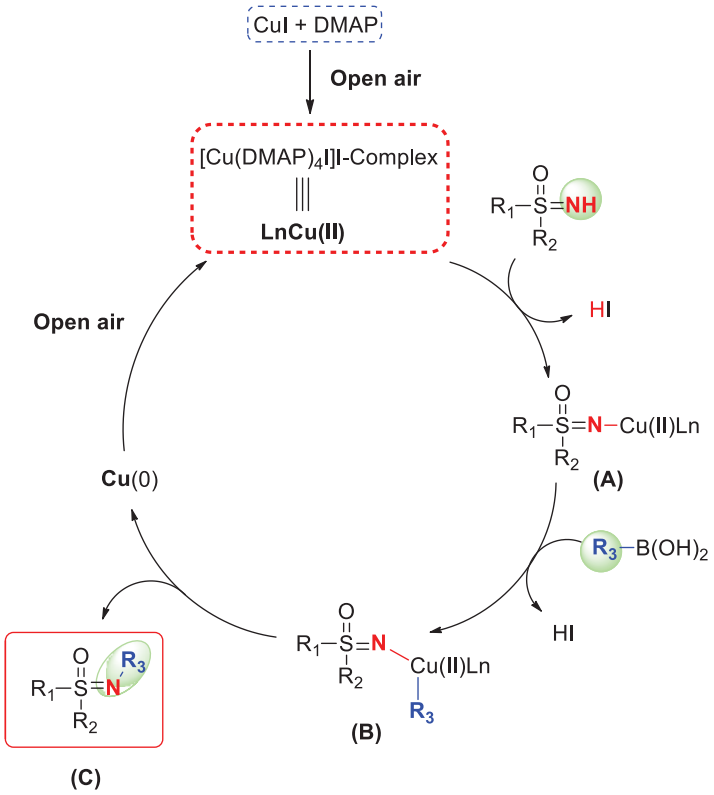
sulfoximine with different vinyl halides under harsh reaction conditions [38, 39]. Nevertheless, vinylboronicacids are important starting materials in organic synthesis and explored for *N*-vinylation of various amines. However, to the best of our knowledge *N*-vinylation of sulfoximine with vinylboronic acid is not reported in the literature. In this context, sulfoximine **1a** was subjected for *N*-vinylation with *trans*-2-phenylvinylboronic acid. To our goodness, the optimized reaction condition was well suited to the task and *N*-vinyl-*S*-methyl-*S*-phenylsulfoximine was obtained in 84% yield within 45 mins at room temperature (**Scheme 4.4**, **3aw**).



Scheme 4.4. *N*-vinylation of *S*-methyl-*S*-phenylsulfoximine using *trans*-2-phenylvinylboronic acid.

4.3 PLAUSIBLE REACTION MECHANISM

The mechanism of *N*-arylation with arylboronic acids *i.e. Chan-Lam* reaction is well documented where the reaction proceeds through three major steps: i) ligand exchange (ii) *trans*-metallation and (iii) reductive elimination. However, the role of 4-DMAP in the *N*-arylation of sulfoximine with strerically hindered arylboronic acid was not clear to us. It is well known that copper (I) as well as copper (II) salts reacts with 4-DMAP and forms more reactive [copper-DMAP] adducts (**Scheme 4.5**) [31, 32].



Scheme 4.5. Proposed mechanism for *N*-arylation of sulfoximine with arylboronic acid.

For instance, the reaction of copper (II) chloride with 4-DMAP leads to the formation of $Cu(DMAP)_4Cl_2$ [31]. Recently, Phukan and co-workers disclosed the reaction of copper(I) iodide with 4-DMAP which provides $Cu[(DMAP)_4I]I$ complex in DMSO [32]. This complex shows excellent catalytic activity in *Chan-Lam* reactions. In light of this, a plausible mechanism has been proposed for *N*-arylation of sulfoximine using arylboronic acids (**Scheme 3.6**). First, CuI and 4-DMAP provides Cu(II)-complex *in situ* under open air condition. This Cu(II)-complex undergoes for ligand exchange with sulfoximine to give intermediate (**A**). Subsequently, arylboronic acid undergoes *trans*-metallation with the complex (**A**) and forms the intermediate (**B**). Finally,the reductive elimination of (**B**) provides the desired *N*-arylated product and copper(0)

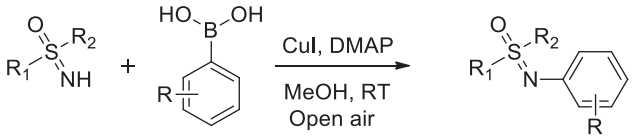
species. Under open air condition, the reduced Cu(I) catalyst re-oxidized to Cu(II) species and catalytic cycle is resumed.

4.4 CONCLUSION

In conclusion, *N*-arylation of sulfoximines with arylboronic acid was demonstrated using catalytic amount of copper(I) iodide and 4-DMAP in methanol at room temperature. A wide range of aryl-alkyl, diaryl, aryl-benzyl, dibenzyl and dialkylsulfoximines were *N*-arylated with library of substituted arylboronic acids bearing electron donating and withdrawing groups in a short span of time. All the reaction took place at room temperature and provided good to excellent yields of *N*-arylsulfoximines. More importantly, *N*-arylation of sulfoximines with sterically hindered arylboronic acid such as 2,4,6-trimethylphenylboronic acid, 2,6-dimethylphenylboronic acid, 2,6-dimethoxyphenylboronic acid and 2,6-flurophenylboronic acid was successfully demonstrated under optimized condition in good yields. 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 condition was well suited to the task of *N*-vinylation of sulfoximine with *trans*-2-phenylvinylboronic acid. Overall, the current methodology appears to be more general from synthetic point of view which will find wide applications in organic synthesis.

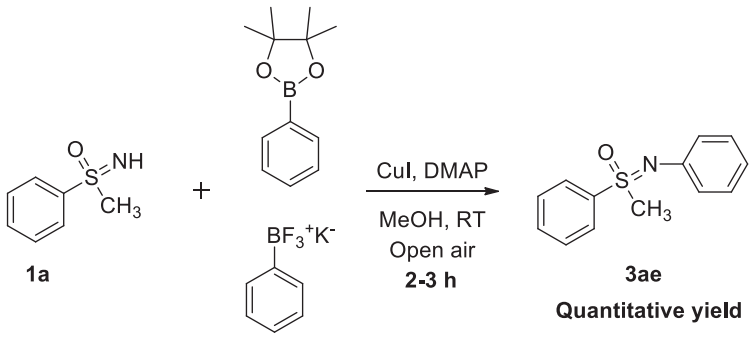
4.5 EXPERIMENTAL SECTION

4.5.1 Experimental procedure for *N*-arylationof sulfoximineswith arylboronicacids



Sulfoximines (150 mg), copper(I) iodide (10 mol%) and 4-DMAP (1 equiv.) was stirred in methanol (2 mL) under open air condition at room temperature for 5 mins. Aryl- or alkylboronic acid (1.5 equiv.) was added to the reaction mixture and allowed to stir at RT. The progress of reaction was monitored on thin layer chromatography. After completion, the reaction mixture was diluted with DCM and washed with distilled water, sodium bicarbonate and brine solution. The organic layer was dried over anhydrous sodium sulfate, filtered and evaporated in rota-evaporator. The crude product was purified in silica-gel column chromatography using ethyl acetate: hexane as eluent to obtain the desired products.

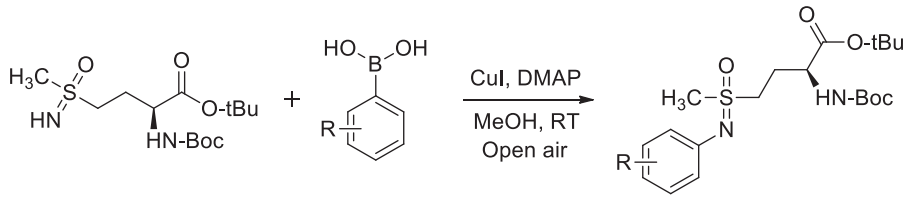
4.5.2 Experimental procedure for *N*-arylation of sulfoximine with boronic acid surrogates



S-Methyl-*S*-phenylsulfoximine (0.967 mmol, 150 mg), copper(I) iodide (10 mol%) and 4-DMAP (1 equiv.) was stirred in methanol (2 mL) at room temperature for

5 mins under open air condition. After that phenylboronic acid surrogate (phenylboronic acid pinacol ester/ potassium phenyltrifluoroborate) (1.5 equiv.) was added to the reaction mixture and allowed to stir at RT until the disappearance of the sulfoximine. The progress of reaction was monitored on thin layer chromatography. After completion, the reaction mixture was diluted with DCM and washed with distilled water, sodium bicarbonate and brine solution. The organic layer was dried over anhydrous sodium sulfate, filtered and evaporated in rota-evaporator. The crude product was purified in silica-gel column chromatography using ethyl acetate:hexane as eluent to obtain the desired product in 80-85% yield.

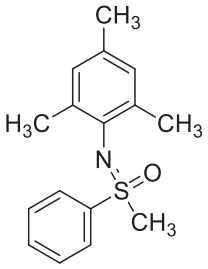
4.5.3 Experimental procedure for *N*-arylation of L-methionine sulfoximine derivative with arylboronic acids



L-Methionine sulfoximine derivative (0.59 mmol, 200 mg), copper(I) iodide (10 mol%) and 4-DMAP (1 equiv.) was stirred in methanol (2 mL) at room temperature for 5 mins under open air condition. After that arylboronic acid (1.5 equiv.) was added to the reaction mixture and allowed to stir at RT until the completion of reaction. The progress of reaction was monitored on thin layer chromatography using 20-40% ethyl acetate:hexane eluent (in *Ninhydrin* Stain). After completion, the reaction mixture was filtered through celite and washed with dichloromethane (DCM) and evaporated in rota-evaporator. The crude product was purified on silica-gel column chromatography using 10-50% ethyl acetate: hexane as eluent to obtain the desired product.

4.6 ANALYTICAL DATA FOR *N*-ARYLSULFOXIMINES:

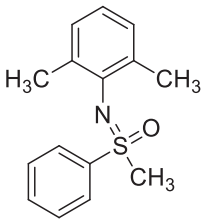
4.6.1 *N*-(2,4,6-trimethylphenyl)-*S*,*S*-methylphenylsulfoximine (3aa)



3aa

The title compound was obtained as pale yellow oil (Yield = 235 mg, 89 %). The product was isolated by silica-gel Column Chromatography using 20% ethyl acetate:hexane as eluent. R_f = 0.25. **IR** (neat, cm^{-1}): 1449, 1232, 1221, 749. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.9 Hz, 2H), 7.59 (m, 3H), 6.84 (s, 2H), 3.02 (s, 3H), 2.33 (s, 6H), 2.23 (s, 3H). **^{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:** Calc. for $C_{16}H_{20}NOS$ $[M+H]^+$: 274.1226 , Obser. 274.1239

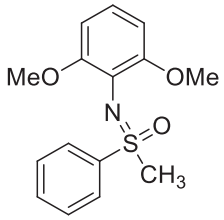
4.6.2 *N*-(2,6-dimethylphenyl)-*S*,*S*-methylphenylsulfoximine (3ab)



3ab

The title compound was obtained as yellow oil (Yield = 210 mg, 84%). The product was isolated by silica-gel Column Chromatography using 20% ethyl acetate:hexane as eluent. R_f = 0.48. **IR** (neat, cm^{-1}): 1474, 1272, 1089, 756, 733. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.5 Hz, 2H), 7.59 (m, 3H), 7.01 (d, *J* = 7.4 Hz, 2H), 6.87 (t, *J* = 7.4 Hz, 1H), 3.03 (s, 3H), 2.36 (s, 6H). **^{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:** Calc. for $C_{15}H_{18}NOS$ $[M+H]^+$: 260.1104, Obser. 260.1093

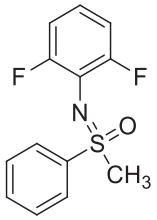
4.6.3 *N*-(2,6-dimethoxyphenyl)-*S,S*-methylphenylsulfoximine (3ac)



3ac

The title compound was obtained as yellow oil (Yield = 228 mg, 81%). The product was isolated by silica-gel Column Chromatography using 40% ethyl acetate:hexane as eluent. R_f = 0.38. **IR** (neat, cm^{-1}):1449, 1284, 1079, 765. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.7 Hz, 2H), 7.52 (m, 3H), 6.87 (t, *J* = 8.3 Hz, 1H), 6.51 (d, *J* = 8.3 Hz, 2H), 3.70 (s, 6H), 3.15 (s, 3H). **^{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:** Calc. for $C_{15}H_{19}NO_3S$ $[M+H]^+$: 292.1002, Obser. 292.0991

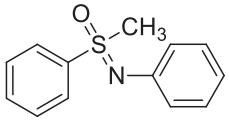
4.6.4 *N*-(2,6-difluorophenyl)-*S,S*-methylphenylsulfoximine (3ad)



3ad

The title compound was obtained as transparent oil. Yield = 103 mg, 40%. The product was isolated by silica-gel Column Chromatography using 30% ethyl acetate:hexane as eluent. R_f = 0.20. **IR** (neat, cm^{-1}):1441, 1249, 1077, 749. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.8 Hz, 2H), 7.65-7.48 (m, 3H), 6.86-6.74 (t, *J* = 8.3 Hz, 3H), 3.25 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$)δ 156.8 (dd, J_{C-F} = 247.6 Hz, J_{C-F} = 5.8 Hz), 140.4, 133.5, 129.5, 128.2, 122.3 (t, J_{C-F} = 9.5 Hz), 111.7 (t, J_{C-F} = 15.6 Hz), 111.5 (dd, J_{C-F} = 18.6 Hz, J_{C-F} = 5.2 Hz), 46.2. **HRMS:** Calc. for $C_{14}H_{16}F_2NOS$ $[M+H]^+$: 284.0921, Obser. 284.0995

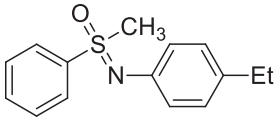
4.6.5 *N*-phenyl-*S*,*S*-methylphenylsulfoximine (3ae)



3ae

The title compound was obtained as white solid (Yield = 207 mg, 93%). The product was isolated by silica-gel Column Chromatography using 30% ethyl acetate:hexane as eluent. Melting point: 100-101 °C. R_f = 0.22. **IR** (KBr, cm^{-1}): 3044, 2089, 1614, 1486, 1267, 1202, 1093, 1040. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94–7.88 (m, 2H), 7.48 (m, 3H), 7.05 (t, *J* = 7.8 Hz, 2H), 6.94 (d, *J* = 7.5 Hz, 2H), 6.80 (t, *J* = 7.3 Hz, 1H), 3.17 (s, 3H). **^{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:** Calc. for $C_{13}H_{14}NOS$ $[M+H]^+$: 232.0796, Obser. 232.0778

4.6.6 *N*-(4-ethylphenyl)-*S*,*S*-methylphenylsulfoximine (3af)

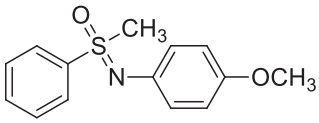


3af

The title compound was obtained as pale yellow oil (Yield = 225 mg, 90%). The product was isolated by silica-gel Column Chromatography using 30% ethyl acetate:hexane as eluent. R_f = 0.28. **IR** (neat, cm^{-1}): 3299, 1615, 1517, 1286, 1225, 1090, 1010, 833. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.7 Hz, 2H), 7.53 (m, 3H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 3.20 (s, 3H), 2.49 (q, *J* = 7.5 Hz, 2H), 1.12 (t, *J* = 7.6 Hz, 3H). **^{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:** Calc. for $C_{15}H_{18}NOS$ $[M+H]^+$: 260.1109, Obser. 260.1100

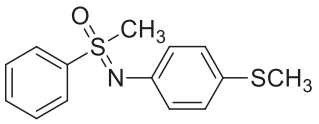
4.6.7 *N*-(4-methoxyphenyl)-*S*,*S*-methylphenylsulfoximine (3ag)



3ag

The title compound was obtained as white solid (Yield = 229 mg, 91 %). Melting point: 102-106 °C. The product was isolated by silica-gel Column Chromatography using 40% ethyl acetate:hexane as eluent. R_f = 0.18. **IR** (KBr, cm^{-1}): 3012, 2930, 2833, 1513, 1444, 1263, 1239, 1042. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99–7.90 (m, 2H), 7.58–7.47 (m, 3H), 6.93 (d, *J* = 9.0 Hz, 2H), 6.66 (d, *J* = 9.0 Hz, 2H), 3.67 (s, 3H), 3.19 (s, 3H). **^{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:** Calc. for $C_{14}H_{16}NO_2S$ $[M+H]^+$: 262.0902, Obser. 262.0887

4.6.8 *N*-(4-thiomethylphenyl)-*S*,*S*-methylphenylsulfoximine (3ah)

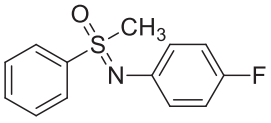


3ah

The title compound was obtained as yellow oil (Yield = 209 mg, 78%). The product was isolated by silica-gel Column Chromatography using 20% ethyl acetate:hexane as eluent. R_f = 0.42. **IR** (neat, cm^{-1}): 3012, 2930, 2833, 1513, 1444, 1263, 1239, 1042. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H),

6.92 (d, J = 8.4 Hz, 2H), 3.21 (s, 3H), 2.35 (s, 3H). **^{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:** Calc. for $C_{14}H_{16}NOS_2$ $[M+H]^+$: 278.0673, Obser. 278.0693

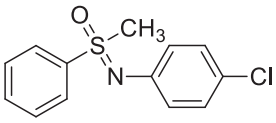
4.6.9 *N*-(4-fluorophenyl)-*S*,*S*-methylphenylsulfoximine (3ai)



3ai

The title compound was obtained as white solid (Yield = 207 mg, 86%). Melting point: 82-86 °C. The product was isolated by silica-gel Column Chromatography using 40% ethyl acetate:hexane as eluent. R_f = 0.28. **IR** (KBr, cm^{-1}): 3053, 3002, 2928, 1445, 1281, 1263, 1208, 1093, 1032, 821, 745, 679. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 (d, J = 7.7 Hz, 2H), 7.48 (m, 3H), 6.88 (d, J = 8.7, 2H), 6.72 (d, J = 8.7 Hz, 2H), 3.15 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 158.3 (d, $J_{C\text{-}F}$ = 239.0), 141.0 (d, $J_{C\text{-}F}$ = 2.6), 139.1, 133.3, 129.6, 128.6, 124.4 (d, $J_{C\text{-}F}$ = 7.7 Hz), 115.5 (d, $J_{C\text{-}F}$ = 22.1 Hz), 46.0. **HRMS:** Calc. for $C_{13}H_{13}FNOS$ $[M+H]^+$: 250.0702, Obser. 250.0687

4.6.10 *N*-(4-chlorophenyl)-*S*,*S*-methylphenylsulfoximine (3aj)

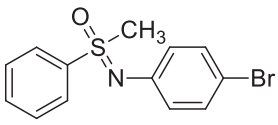


3aj

The title compound was obtained as white solid (Yield = 226 mg, 88%). Melting point: 64-66 ºC. The product was isolated by silica-gel Column Chromatography using 40% ethyl acetate:hexane as eluent. R_f = 0.38. **IR** (KBr, cm^{-1}):

3064, 3014, 2926, 1487, 1402, 1371, 1291, 1198, 1091, 738, 681. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.9 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.02 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 3.20 (s, 3H). **^{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:** Calc. for $C_{13}H_{13}ClNOS$ $[M+H]^+$: 266.0406, Obser. 266.0396

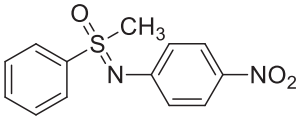
4.6.11 *N*-(4-bromophenyl)-*S*,*S*-methylphenylsulfoximine (3ak)



3ak

The title compound was obtained as white solid (Yield = 266 mg, 89%). Melting point: 109-111 °C. The product was isolated by silica-gel Column Chromatography using 30% ethyl acetate:hexane as eluent. R_f = 0.44. **IR** (KBr, cm^{-1}): 3109, 3026, 2926, 1485, 1401, 1267, 1203, 1007, 821, 732. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.9 Hz, 2H), 7.53 (m, 3H), 7.17 (d, *J* = 8.2 Hz, 2H), 6.85 (d, *J* = 8.2 Hz, 2H), 3.21 (s, 3H). **^{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:** Calc. for $C_{13}H_{13}BrNOS$ $[M+H]^+$: 309.9901, Obser. 309.9896

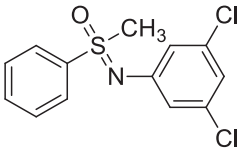
4.6.12 *N*-(4-nitrophenyl)-*S*,*S*-methylphenylsulfoximine (3al)



3al

The title compound was obtained as yellow solid (Yield = 221 mg, 83%). Melting point: 149-150 ºC. The product was isolated by silica-gel Column Chromatography using 40% ethyl acetate:hexane as eluent. R_f = 0.22. **IR** (KBr, cm^{-1}): 3097, 3020, 2913, 1592, 1294, 1050, 1013. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.7 Hz, 2H), 7.91 (d, *J* = 7.9 Hz, 2H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 3.29 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 152.8, 141.7, 138.2, 134.1, 130.0, 128.5, 126.3, 125.3, 122.5, 115.8, 46.6. **HRMS:** Calc. for $C_{13}H_{13}N_2O_3S$ $[M+H]^+$: 277.0647, Obser. 277.0637

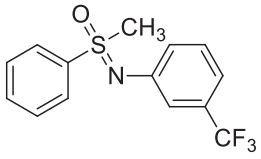
4.6.13 *N*-(3,5-dichlorophenyl)-*S*,*S*-methylphenylsulfoximine (3am)



3am

The title compound was obtained as white solid (Yield = 249 mg, 86%). Melting point: 83ºC. The product was isolated by silica-gel Column Chromatography using 30% ethyl acetate:hexane as eluent. R_f = 0.40. **IR** (KBr, cm^{-1}):3109, 3026, 2926, 1485, 1401. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.8 Hz, 2H), 7.62–7.51 (m, 3H), 6.87 (s, 2H), 6.81 (s, 1H), 3.22 (s, 3H). **^{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:** Calc. for $C_{13}H_{12}Cl_2NOS$ $[M+H]^+$: 300.0017, Obser. 300.0011

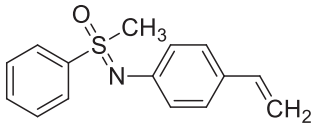
4.6.14 *N*-(3-trifluoromethylphenyl)-*S*,*S*-methylphenylsulfoximine (3an)



3an

The title compound was obtained as pale yellow oil (Yield = 254 mg, 88%). The product was isolated by silica-gel Column Chromatography using 30% ethyl acetate:hexane as eluent. R_f = 0.28. **IR** (neat, cm^{-1}): 3129, 3016, 2936, 1486, 1401. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.8 Hz, 2H), 7.63 (t, *J* = 7.3 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 2.9 Hz, 1H), 7.24–7.09 (m, 3H), 3.28 (s, 3H). **^{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:** Calc. for $C_{14}H_{13}F_3NOS$ $[M+H]^+$: 300.0670, Obser. 300.0656

4.6.15 *N*-(4-vinylphenyl)-*S*,*S*-methylphenylsulfoximine (3ao)

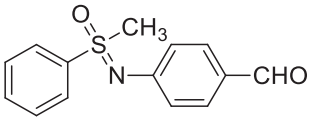


3ao

The title compound was obtained as pale yellow oil (Yield = 203 mg, 82%). The product was isolated by silica-gel Column Chromatography using 30% ethyl acetate:hexane as eluent. R_f = 0.16. **IR** (neat, cm^{-1}): 3022, 2910, 2833, 1622, 1513, 1263, 1239, 1042. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.8 Hz, 2H), 7.53 (dt, *J* = 32.7, 7.5 Hz, 3H), 7.16 (d, *J* = 8.3 Hz, 2H), 6.95 (d, *J* = 8.3 Hz, 2H), 6.55 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.53 (d, *J* = 17.6 Hz, 1H), 5.04 (d, *J* = 10.9 Hz, 1H), 3.22 (s, 3H). **^{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:** Calc. for $C_{15}H_{16}NOS$ $[M+H]^+$: 258.0953, Obser.258.0958

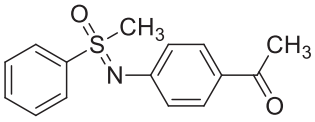
4.6.16 *N*-(4-formylphenyl)-*S,S*-methylphenylsulfoximine (3ap)



3ap

The title compound was obtained as pale yellow solid (Yield = 151 mg, 60%). Melting point: 92-94 ºC. The product was isolated by silica-gel Column Chromatography using 40% ethyl acetate:hexane as eluent. R_f = 0.38. **IR** (KBr, cm^{-1}): 3001, 2921, 2836, 1688, 1595. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.75 (s, 1H), 7.93 (d, *J* = 7.8 Hz, 2H), 7.60 (t, *J* = 6.9 Hz, 3H), 7.53 (t, *J* = 7.7 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 3.28 (s, 3H). **^{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:** Calc. for $C_{14}H_{14}NO_2S$ $[M+H]^+$: 260.0745, Obser. 260.0736

4.6.17 *N*-(4-acetylphenyl)-*S,S*-methylphenylsulfoximine (3aq)

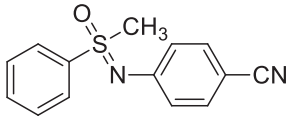


3aq

The title compound was obtained as brown solid (Yield = 119 mg, 45%). Melting point: 86-87 °C. The product was isolated by silica-gel Column Chromatography using 40% ethyl acetate:hexane as eluent. R_f = 0.22. **IR** (KBr, cm^{-1}):3001, 2911, 2836, 1725, 1597. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.7 Hz, 2H), 7.71 (d, *J* = 8.5 Hz,

2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 3.26 (s, 3H), 2.45 (s, 3H). **^{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:** Calc. for $C_{15}H_{16}NO_2S$ $[M+H]^+$: 274.0902, Obser. 274.0892

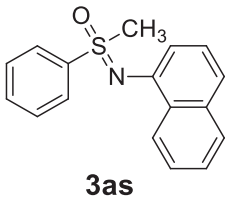
4.6.18 *N*-(4-cyanophenyl)-*S*,*S*-methylphenylsulfoximine (3ar)



3ar

The title compound was obtained as pale yellow oil (Yield = 99 mg, 40%). The product was isolated by silica-gel Column Chromatography using 40% ethyl acetate:hexane as eluent. R_f = 0.24. **IR** (neat, cm^{-1}): 3030, 2930, 2217, 1601, 1490, 1298. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.9 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 6.98 (d, *J* = 8.3 Hz, 2H), 3.27 (s, 3H). **^{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:** Calc. for $C_{14}H_{13}N_2OS$ $[M+H]^+$: 257.0749, Obser. 257.0737

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

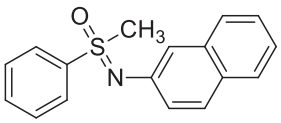


3as

The title compound was obtained as brown oil (Yield = 244 mg, 90%). The product was isolated by silica-gel Column Chromatography using 30% ethyl acetate:hexane

as eluent. R_f = 0.22. **IR** (neat, cm^{-1}): 3065, 3019, 2923, 1511, 1481, 1282, 1191, 1059. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.2 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 2H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.56–7.44 (m, 5H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 7.4 Hz, 1H), 3.32 (s, 3H). **^{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:** Calc. for $C_{17}H_{16}NOS$ $[M+H]^+$: 282.0953, Obser. 282.0942

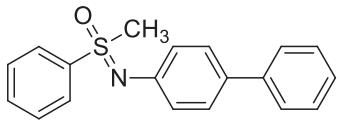
4.6.20 *N*-(2-naphthyl)-*S*,*S*-methylphenylsulfoximine (3at)



3at

The title compound was obtained as brown solid (Yield = 231 mg, 85%). Melting point: 91-92 °C. The product was isolated by silica-gel Column Chromatography using 30% ethyl acetate:hexane as eluent. R_f = 0.26. **IR** (KBr, cm^{-1}): 3012, 2930, 1521, 1499, 1316, 1298, 1246, 1080, 1013. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.2 Hz, 2H), 7.54–7.31 (m, 6H), 7.24 (s, 1H), 7.17 (t, *J* = 6.9 Hz, 1H), 7.10 (d, *J* = 7.7 Hz, 2H), 3.12 (s, 3H). **^{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:** Calc. for $C_{17}H_{16}NOS$ $[M+H]^+$: 282.0953, Obser. 282.0940

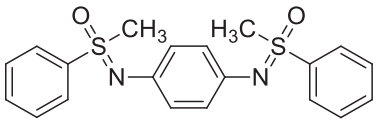
4.6.21 *N*-(4-benzylphenyl)-*S*,*S*-methylphenylsulfoximine (3au)



3av

The title compound was obtained as white solid (Yield = 154 mg, 52%). Melting point: 140-141 °C. The product was isolated by silica-gel Column Chromatography using 30% ethyl acetate:hexane as eluent. R_f = 0.14. **IR** (KBr, cm^{-1}): 3015, 3019, 2923, 1599, 1511, 1481, 1281, 836. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.6 Hz, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.54–7.47 (m, 4H), 7.38–7.33 (m, 4H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 3.24 (s, 3H). **^{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:** Calc. for $C_{19}H_{18}NOS$ $[M+H]^+$: 308.1109, Obser. 308.1103

4.6.22 *N*,*N′*-(1,4-phenylene)-bis-*S*,*S*-methylphenylsulfoximine (3av)

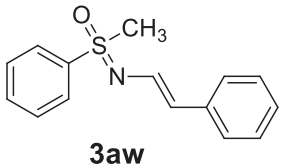


3av

The title compound was obtained as brown oil (Yield = 297 mg, 40%). The product was isolated by silica-gel Column Chromatography using 50-60 % ethyl acetate:hexane as eluent. R_f = 0.20. **IR** (neat, cm-1):3075, 3021, 2933, 1609, 1511, 1481, 1381, 736. **^{1}H NMR** (500 MHz, CDCl3) δ 8.00 (d, *J* = 7.4 Hz, 1H), 7.90 (d, *J* = 6.5 Hz, 3H), 7.63–7.58 (m, 1H),

7.54 (t, *J*= 7.3 Hz, 3H), 7.47 (t, *J* = 7.2 Hz, 3H), 6.76 (d, *J* = 5.5 Hz, 3H), 3.12 (d, *J* = 28.1 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 139.6, 139.2, 133.3, 133.2, 129.6, 129.5, 128.8, 127.9, 124.1, 124.0, 46.3, 45.9. **HRMS:** Calc. for $C_{20}H_{21}N_2O_2S_2$ $[M+H]^+$: 385.1039, Obser. 385.1032

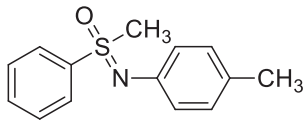
4.6.23 *N*-phenylethynyl-*S*,*S*-methylphenylsulfoximine (3aw)



3aw

The title compound was obtained as brown oil (Yield = 209 mg, 84%). The product was isolated by silica-gel Column Chromatography using 30% ethyl acetate:hexane as eluent. R_f = 0.36. **IR** (neat, cm^{-1}): 1698, 1636, 1217, 1096, 983, 739, 695. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.3 Hz, 2H), 7.63 (t, *J* = 6.9 Hz, 1H), 7.57 (t, *J* = 7.3 Hz, 2H), 7.16 (m, 4H), 7.04 (m, 1H), 6.90 (d, *J* = 13.6 Hz, 1H), 6.19 (d, *J* = 13.6 Hz, 1H), 3.20 (s, 3H). **^{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:** Calc. for $C_{15}H_{16}NOS$ $[M+H]^+$: 258.0953, Obser. 258.0930

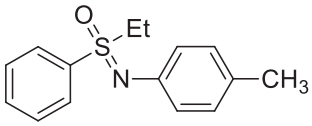
4.6.24 *N*-(4-methylphenyl)-*S*,*S*-methylphenylsulfoximine (3ay)



3ay

The title compound was obtained as white solid (Yield = 215 mg, 91%). Melting point: 112-114 °C. The product was isolated by silica-gel Column Chromatography using 30% ethyl acetate:hexane as eluent. R_f = 0.18. **IR** (KBr, cm^{-1}): 3020, 2923, 1498, 1504, 1287, 1263, 1091, 1069, 1034. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.8 Hz, 2H), 7.52 (m, 3H), 6.90 (s, 4H), 3.20 (s, 3H), 2.18 (s, 3H). **^{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:** Calc. for $C_{14}H_{16}NOS$ $[M+H]^+$: 246.0953, Obser. 246.0940

4.6.25 *N*-(4-methylphenyl)-*S*,*S*-ethylphenylsulfoximine (3by)

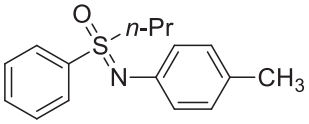


3by

The title compound was obtained as brown solid (Yield = 230 mg, 92%). Melting point: 86 °C. The product was isolated by silica-gel Column Chromatography using 30% ethyl acetate:hexane as eluent. R_f = 0.24. **IR** (KBr, cm^{-1}): 3369, 3057, 2929, 2786, 2359, 2048, 1594, 1487, 1394, 1265, 1193, 1093. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.9 Hz, 2H), 7.52 (m, 3H), 6.90 (s, 4H), 3.30 (m, 2H),

2.18 (s, 3H), 1.27 (t, *J* = 7.4 Hz, 3H). **^{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:** Calc. for $C_{15}H_{18}NOS$ $[M+H]^+$: 260.1109, Obser. 260.1102

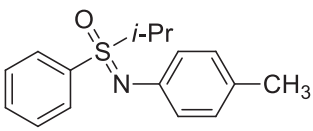
4.6.26 *N*-(4-methylphenyl)-*S,S*-phenylpropylsulfoximine (3cy)



3cy

The title compound was obtained as white solid (Yield = 243 mg, 92%). Melting point: 110 °C. The product was isolated by silica-gel Column Chromatography using 30% ethyl acetate:hexane as eluent. R_f = 0.22. **IR** (KBr, cm^{-1}): 3020, 2923, 1505, 1287, 1263, 1094, 1069, 1034. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.6 Hz, 2H), 7.51 (m, 3H), 6.89 (s, 4H), 3.28 (m, 1H), 3.23–3.16 (m, 1H), 2.17 (s, 3H), 1.76 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). **^{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:** Calc. for $C_{16}H_{20}NOS$ $[M+H]^+$: 274.1266, Obser. 274.1283

4.6.27 *N*-(4-methylphenyl)-*S,S-iso*-propylphenylsulfoximine (3dy)

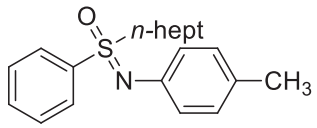


3dy

The title compound was obtained as pale yellow oil (Yield = 230 mg, 87%). The product was isolated by silica-gel Column Chromatography using 20% ethyl acetate:hexane as eluent. R_f = 0.34. **IR** (neat, cm^{-1}):

3020, 2923, 1505, 1287, 1263, 1094, 1069, 1034. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.5 Hz, 2H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 2H), 6.89 (s, 4H), 3.39 (m, 1H), 2.17 (s, 3H), 1.40 (d, *J* = 6.6 Hz, 3H), 1.26 (d, *J* = 6.6 Hz, 3H). **^{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:** Calc. for $C_{16}H_{19}NaNOS$ $[M+Na]^+$: 296.1085, Obser. 296.1097

4.6.28 *N*-(4-methylphenyl)-*S*,*S*-heptylphenylsulfoximine (3ey)

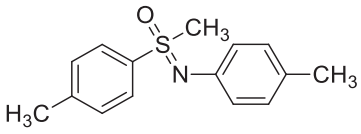


3ey

The title compound was obtained as white solid (Yield = 286 mg, 90%). Melting point: 76 °C. The product was isolated by silica-gel Column Chromatography using 10% ethyl acetate:hexane as eluent. R_f = 0.50. **IR** (KBr, cm^{-1}): 3272, 2927, 1445, 1223, 1110, 991, 752, 689. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.1 Hz, 2H), 7.54-7.46 (m, 3H), 6.90 (s, 4H), 3.34–3.28 (m, 1H), 3.24–3.18 (m, 1H), 2.17 (s, 3H), 1.79–1.78 (m, 1H), 1.67-1.65 (m, 1H), 1.33–1.15 (m, 8H), 0.83 (t, *J* = 6.8 Hz, 3H). **^{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:** Calc. for $C_{13}H_{13}NOS$ $[M+H]^+$: 231.0718,

Obser. 231.0701

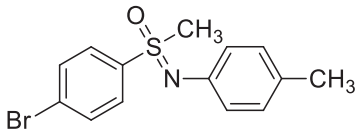
4.6.29 *N*-(4-methylphenyl)-*S*,*S*-(4-methylphenyl)methylsulfoximine (3fy)



3fy

The title compound was obtained as pale yellow viscous oil (Yield = 204 mg, 89%). The product was isolated by silica-gel Column Chromatography using 20% ethyl acetate:hexane as eluent. R_f = 0.40. **IR** (neat, cm^{-1}): 3021, 2922, 1505, 1288, 1197, 1093, 1033, 1013. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 6.90 (s, 4H), 3.18 (s, 3H), 2.38 (s, 3H), 2.18 (s, 3H). **^{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:** Calc. for $C_{15}H_{18}NOS$ $[M+H]^+$: 260.1109, Obser. 260.1149

4.6.30 *N*-(4-methylphenyl)-*S*,*S*-(4-bromophenyl)methylsulfoximine (3gy)

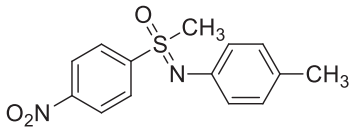


3gy

The title compound was obtained as white solid (Yield = 191 mg, 92%). Melting point: 150 °C. The product was isolated by silica-gel Column Chromatography using 30% ethyl acetate:hexane as eluent. R_f = 0.36. **IR** (neat, cm^{-1}): 3026, 2926, 1588, 1486, 1288, 1201, 1094, 1030. **^{1}H NMR** (500 MHz, CDCl3) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.3

Hz, 2H), 6.91 (d, *J* = 8.1 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 3.20 (s, 3H), 2.19 (s, 3H). **^{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:** Calc. for $C_{14}H_{15}BrNOS$ $[M+H]^+$: 324.0058, Obser. 324.0056

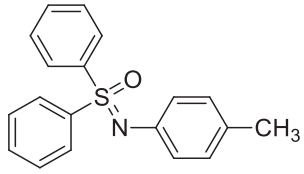
4.6.31 *N*-(4-methylphenyl)-*S*,*S*-methyl-(4-nitrophenyl)sulfoximine (3hy)



3hy

The title compound was obtained as yellow solid (Yield = 198 mg, 91%). Melting point: 85 °C. The product was isolated by silica-gel Column Chromatography using 20% ethyl acetate:hexane as eluent. R_f = 0.28. **IR** (KBr, cm^{-1}): 3094, 3029, 2932, 1529, 1348, 1294, 1089, 1041. **^{1}H NMR** (500 MHz, CDCl3) δ 8.33 (d, *J* = 8.5 Hz, 2H), 8.13 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 8.1 Hz, 2H), 6.86 (d, *J* = 8.0 Hz, 2H), 3.27 (s, 3H), 2.18 (s, 3H). **^{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:** Calc. for $C_{14}H_{15}N_2O_3S$ $[M+H]^+$: 291.0803, Obser. 291.0804

4.6.32 *N*-(4-methylphenyl)-*S*,*S*-diphenylsulfoximine (3iy)

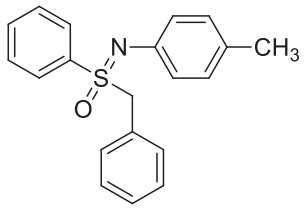


3iy

The title compound was obtained as white solid (Yield = 178 mg, 84%). Melting point: 171 °C. The product was isolated by silica-gel Column

Chromatography using 20% ethyl acetate:hexane as eluent. R_f = 0.52. **IR** (KBr, cm^{-1}):3083, 2905, 2877, 2381, 2341, 1467, 1286, 1208, 1119, 1104, 1093 748. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.6 Hz, 4H), 7.50–7.41 (m, 6H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 7.9 Hz, 2H), 2.19 (s, 3H). **^{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:** Calc. for $C_{19}H_{18}NOS$ $[M+H]^+$: 308.1109, Obser. 308.1100

4.6.33 *N*-(4-methylphenyl)-*S*,*S*-benzylphenylsulfoximine (3jy)

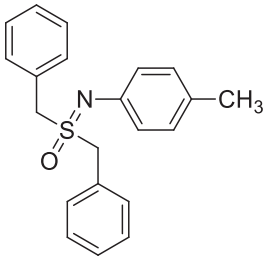


3jy

The title compound was obtained as pale yellow solid (Yield = 173 mg, 83%). Melting point: 148-151 °C. The product was isolated by silica-gel Column Chromatography using 20% ethyl acetate:hexane as eluent. R_f = 0.46. **IR** (KBr, cm^{-1}): 3054, 2917, 2847, 2364, 2333, 1454, 1298, 1218, 1136, 1101, 1096 743. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.9 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 2H), 6.99–6.91 (m, 6H), 4.51 (q, *J* = 13.7 Hz, 2H), 2.20 (s, 3H). **^{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:** Calc. for $C_{20}H_{19}NaNOS$ $[M+Na]^+$: 344.1085, Obser. 344.1070

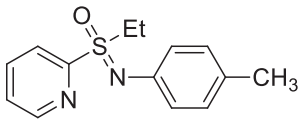
4.6.34 *N*-(4-methylphenyl)-*S,S*-dibenzylsulfoximine (3ky)



3ky

The title compound was obtained as pale yellow solid (Yield = 169 mg, 81%). Melting point: 86 °C. The product was isolated by silica-gel Column Chromatography using 20% ethyl acetate:hexane as eluent. R_f = 0.44. **IR** (KBr, cm^{-1}) 3275, 3105, 3062, 3010, 2996, 2908, 1504,1438, 1406, 1242, 1116, 1063, 1037, 760, 698, 580. **^{1}H NMR** (500 MHz, CDCl3) δ 7.34 (d, *J* = 6.2 Hz, 10H), 7.02–6.96 (m, 4H), 4.31 (d, *J* = 14.1 Hz, 2H), 4.25 (d, *J* = 14.0 Hz, 2H), 2.26 (s, 3H). **^{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:** Calc. for $C_{21}H_{22}NOS$ $[M+H]^+$: 336.1422, Obser. 336.1408

4.6.35 *N*-(4-methylphenyl)-*S,S*-ethyl-(2-pyridyl)sulfoximine (3ly)

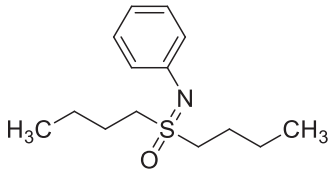


3ly

The title compound was obtained as pale yellow solid (Yield = 213 mg, 93%). Melting point: 165°C. The product was isolated by silica-gel Column

Chromatography using 20-30% ethyl acetate:hexane as eluent. R_f = 0.46. **IR** (KBr, cm^{-1}): 3364, 3047, 2898, 2781, 2354, 2038, 1589, 1483, 1388, 1261, 1184, 1091,973, 814, 757. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.70 (d, *J* = 4.2 Hz, 1H), 8.08 (d, *J* = 7.8 Hz, 1H), 7.84 (t, *J* = 7.7 Hz, 1H), 7.45–7.40 (m, 1H), 6.94–6.86 (m, 4H), 3.65 (dq, *J* = 14.7, 7.4 Hz, 1H), 3.55 (dq, *J* = 14.7, 7.5 Hz, 1H), 2.17 (s, 3H), 1.28 (t, *J* = 7.4 Hz, 3H). **^{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:** Calc. for $C_{14}H_{17}N_2OS$ $[M+H]^+$: 261.1062, Obser. 261.1073

4.6.36 *N*-phenyl-*S*,*S*-dibutylsulfoximine (4a)

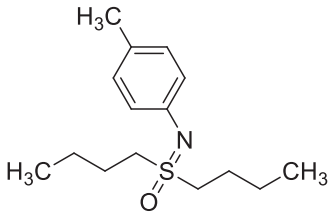


4a

The title compound was obtained as yellow viscous oil (Yield = 197 mg, 92%). The product was isolated by silica-gel Column Chromatography using 10% ethyl acetate:hexane as eluent. R_f = 0.42. **IR** (neat, cm^{-1}): 3048, 2097, 1624, 1573, 1479, 1319, 1274, 1201, 1160, 1079, 943, 841. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.18 (t, *J* = 7.8 Hz, 2H), 7.06 (d, *J* = 7.4 Hz, 2H), 6.91 (t, *J* = 7.3 Hz, 1H), 3.17–3.06 (m, 4H), 1.83-1.76 (m, 4H), 1.43–1.37 (m, 4H), 0.91 (t, *J* = 7.3 Hz, 6H). **^{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:** Calc. for $C_{14}H_{24}NOS$ $[M+H]^+$: 254.1579, Obser. 254.1571

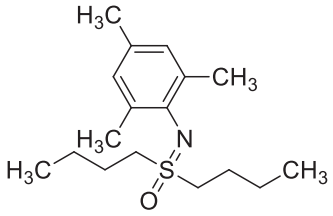
4.6.37 *N*-(4-methylphenyl)-*S,S*-dibutylsulfoximine (4b)



4b

The title compound was obtained as transparent oil (Yield = 205 mg, 91%). The product was isolated by silica-gel Column Chromatography using 10% ethyl acetate:hexane as eluent. R_f = 0.38. **IR** (neat, cm^{-1}): 3272, 3018, 2940, 1724, 1486, 1380, 1242, 1101, 1071, 1036, 807, 729. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.99 (d, *J* = 8.3 Hz, 2H), 6.95 (d, *J* = 8.3 Hz, 2H), 3.17–3.03 (m, 4H), 2.25 (s, 3H), 1.82–1.76 (m, 4H), 1.44–1.36 (m, 4H), 0.83 (t, *J* = 7.4 Hz, 6H). **^{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:** Calc. for $C_{15}H_{26}NOS$ $[M+H]^+$: 268.1735, Obser. 268.1755.

4.6.38 *N*-(2,4,6-trimethylphenyl)-*S,S*-dibutylsulfoximine (4c)

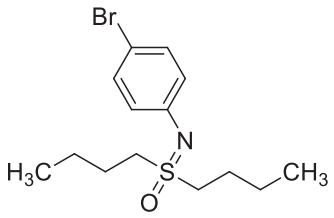


4c

The title compound was obtained as pale yellow viscous oil (Yield = 177 mg, 71%). The product was isolated by silica-gel Column Chromatography using 10% ethyl acetate:hexane as eluent. R_f = 0.34. **IR** (neat, cm^{-1}): 3272, 2960, 1724, 1466, 1380, 1242,

1101, 1016, 807, 729. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.79 (s, 2H), 3.07-2.97 (m, 4H), 2.27 (s, 6H), 2.20 (s, 3H), 1.84-1.78 (m, 4H), 1.43–1.39 (m, 4H), 0.92 (t, *J* = 7.3 Hz, 6H). **^{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:** Calc. for $C_{17}H_{30}NOS$ $[M+H]^+$: 296.2048, Obser. 296.2078

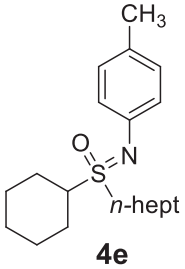
4.6.39 *N*-(4-bromophenyl)-*S*,*S*-dibutylsulfoximine (4d)



4d

The title compound was obtained as pale yellow oil (Yield = 250 mg, 89%). The product was isolated by silica-gel Column Chromatography using 40% ethyl acetate:hexane as eluent. R_f = 0.38. **IR** (neat, cm^{-1}): 3272, 3020, 2960, 1726, 1476, 1381, 1262, 1101, 1056, 1002, 807, 729. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 3.16–3.04 (m, 4H), 1.81-1.76 (m, 4H), 1.43–1.38 (m, 4H), 0.91 (t, *J* = 7.3 Hz, 6H). **^{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:** Calc. for $C_{14}H_{23}BrNOS$ $[M+H]^+$: 332.0684, Obser. 332.0664

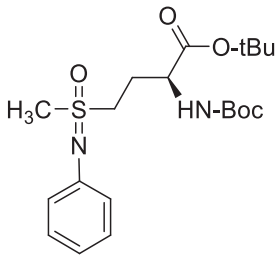
4.6.40 *N*-(4-methylphenyl)-*S*,*S*-cyclohexylheptylsulfoximine (4e)



4e

The title compound was obtained as yellow oil (Yield = 170 mg, 83%). The product was isolated by silica-gel Column Chromatography using 15 % ethyl acetate:hexane as eluent. R_f = 0.24. **IR** (neat, cm^{-1}): 3310, 2920, 2875, 2814, 2313, 1981, 1504, 1644, 1450, 1277, 1129, 1094, 1034, 958, 849, 773, 690. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.97 (s, 4H), 3.10–3.04 (m, 2H), 3.02–2.96 (m, 1H), 2.33–2.15 (m, 3H), 2.24 (s, 3H), 1.91-1.89 (m, 2H), 1.81–1.75 (m, 2H), 1.69 (d, *J* = 12.2 Hz, 1H), 1.64–1.48 (m, 2H), 1.33-1.23 (m, 10H), 0.84 (t, *J* = 6.8 Hz, 3H). **^{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:** Calc. for $C_{20}H_{35}NOS$ $[M+H]^+$: 337.2439, Obser. 337.2425.

4.6.41 L-Methionine Sulfoximine Derivative (4f)

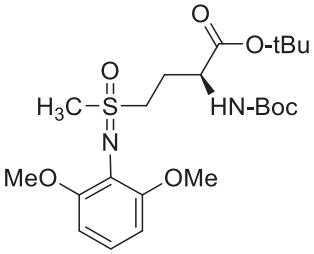


4f

The title compound was obtained as transparent oil (Yield = 223 mg, 91%). The product was isolated by silica-gel Column Chromatography using 40 % ethyl acetate:hexane as eluent and product spot was identified on TLC using *Ninhydrin* stain. R_f = 0.18. **IR** (neat, cm^{-1}): 3845, 3322,

2941, 2817, 2641, 2320, 2082, 1717, 1610, 1529, 1486, 1233, 1202, 1088, 1047, 853, 744. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.19 (t, *J* = 6.9 Hz, 2H), 7.04 (t, *J* = 7.0 Hz, 2H), 6.94 (t, *J* = 7.2 Hz, 1H), 5.26 (s, 1H), 4.22 (s, 1H), 3.38–3.16 (m, 2H), 3.03 (s, 3H), 2.43-2.40 (m, 1H), 2.20-2.10 (m, 1H), 1.41 (d, *J* = 7.4 Hz, 18H). **^{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:** Calc. for $C_{20}H_{34}N_2O_5S$ $[M+H]^+$: 413.2105, Obser. 413.2104

4.6.42 L-Methionine Sulfoximine Derivative (4g)

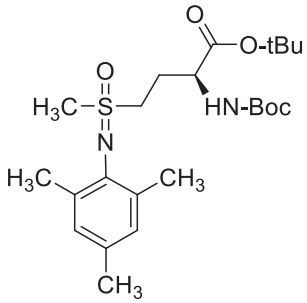


4g

The title compound was obtained as transparent oil (Yield = 219 mg, 78%). The product was isolated by silica-gel Column Chromatography using 40% ethyl acetate:hexane as eluent and product spot was identified on TLC using *Ninhydrin* stain. R_f = 0.24. **IR** (neat, cm^{-1}): 3842, 3321, 2976, 2941, 2837, 2641, 2320, 2082, 1717, 1529, 1446, 1271, 1223, 1148, 1087, 853, 766, 744. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.91 (t, *J* = 8.2 Hz, 1H), 6.54 (d, *J* = 8.2 Hz, 2H), 5.42-5.19 (m, 1H), 4.25 (s, 1H), 3.81 (s, 6H), 3.32-3.22 (m, 2H), 3.05 (d, *J* = 9.0 Hz, 3H), 2.45 (d, *J* = 5.1 Hz, 1H), 2.27-2.22 (m, 1H), 1.43 (d, *J* = 8.2 Hz, 18H).

^{13}C NMR (125 MHz, CDCl3) 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:** Calc. for $C_{22}H_{38}N_2O_7S$ $[M+H]^+$: 473.2316, Obser. 473.2315

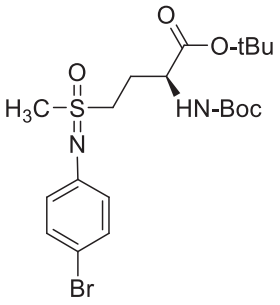
4.6.43 L-Methionine Sulfoximine Derivative (4h)



4h

The title compound was obtained as transparent oil (Yield = 213 mg, 79%). The product was isolated by silica-gel Column Chromatography using 30% ethyl acetate:hexane as eluent and product spot was identified on TLC using *Ninhydrin* stain. R_f = 0.24. **IR** (neat, cm^{-1}): 3845, 3322, 2941, 2817, 2641, 2320, 2082, 1717, 1529, 1446, 1223, 1148, 1047, 853, 744. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.80 (s, 2H), 5.27-5.20 (m, 1H), 4.24 (s, 1H), 3.33–3.14 (m, 2H), 2.89 (s, 3H), 2.49–2.40 (m, 1H), 2.24 (s, 6H), 2.20 (s, 3H), 2.17–2.11 (m, 1H), 1.44– 1.42 (m, 18H). **^{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:** Calc. for $C_{23}H_{40}N_2O_5S$ $[M+H]^+$: 455.2574, Obser. 455.2576

4.6.44 L-Methionine Sulfoximine Derivative (4i)



4i

The title compound was obtained as transparent liquid (Yield = 260 mg, 89%). The product was isolated by silica-gel Column Chromatography using 40% ethyl acetate:hexane as eluent and product spot was identified on TLC using *Ninhydrin* stain. R_f = 0.20. **IR** (neat, cm^{-1}): 3845, 3322, 2981, 2856, 2641, 2320, 2082, 1717, 1529, 1476, 1263, 1201, 1142, 1047, 1004, 853, 744. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.5 Hz, 2H), 6.91 (d, *J* = 7.7 Hz, 2H), 5.26 (s, 1H), 4.21 (s, 1H), 3.33–3.17 (m, 2H), 3.01 (s, 3H), 2.40-2.35 (m, 1H), 2.13–2.06 (m, 1H), 1.42–1.40 (m, 18H). **^{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:** Calc. for $C_{20}H_{33}BrN_2O_5S$ $[M+H]^+$: 491.1210, Obser. 419.1204

4.7 SPECTRAL DATA FOR FEW PRODUCTS

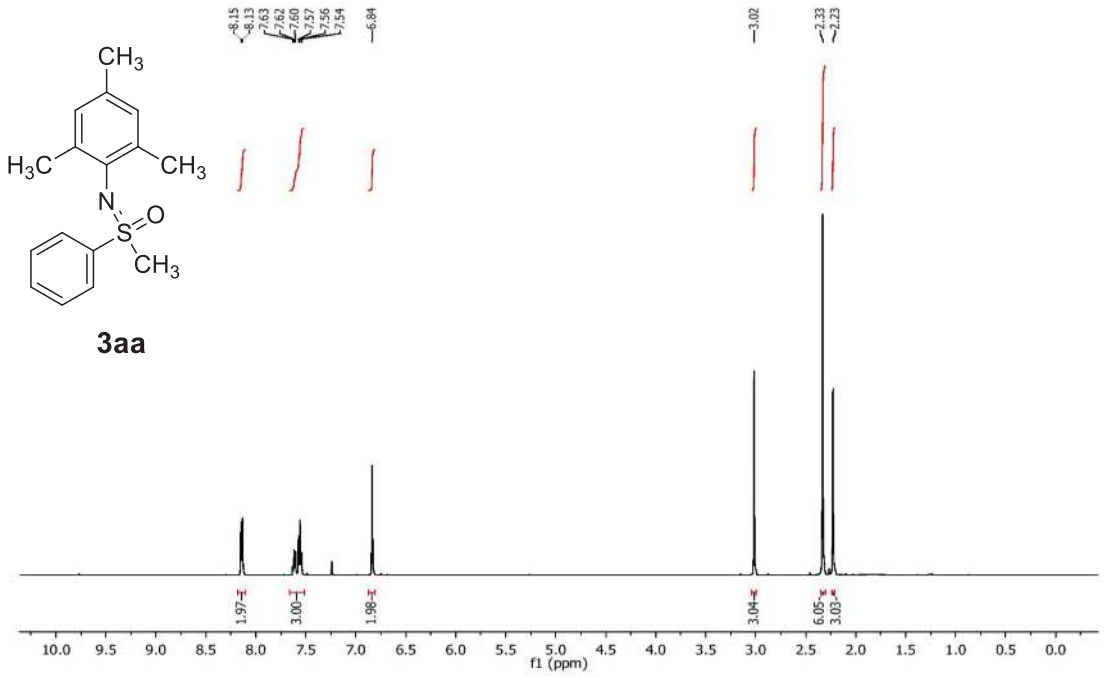


Figure 4.2 ^{1}H NMR of *N*-(2,4,6-trimethylphenyl)-*S,S*-methylphenylsulfoximine (**3aa**)

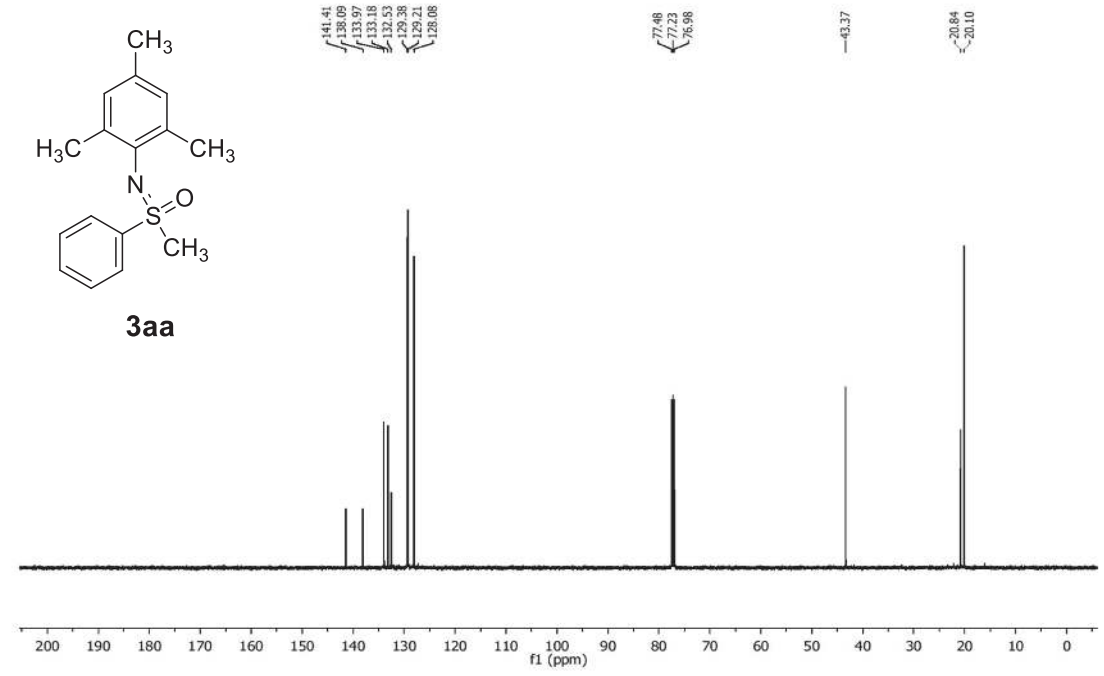


Figure 4.3 ^{13}C NMR of *N*-(2,4,6-trimethylphenyl)-*S,S*-methylphenylsulfoximine (**3aa**)

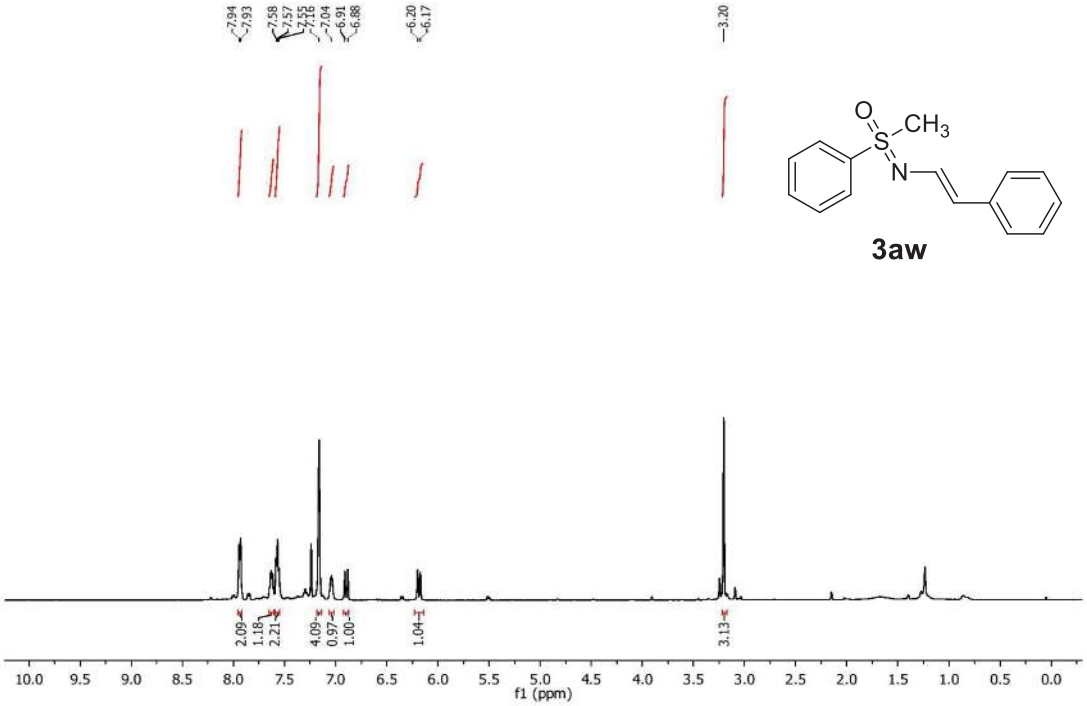


Figure 4.4 ^{1}H NMR of *N*-phenylethynyl-*S,S*-methylphenylsulfoximine (**3aw**)

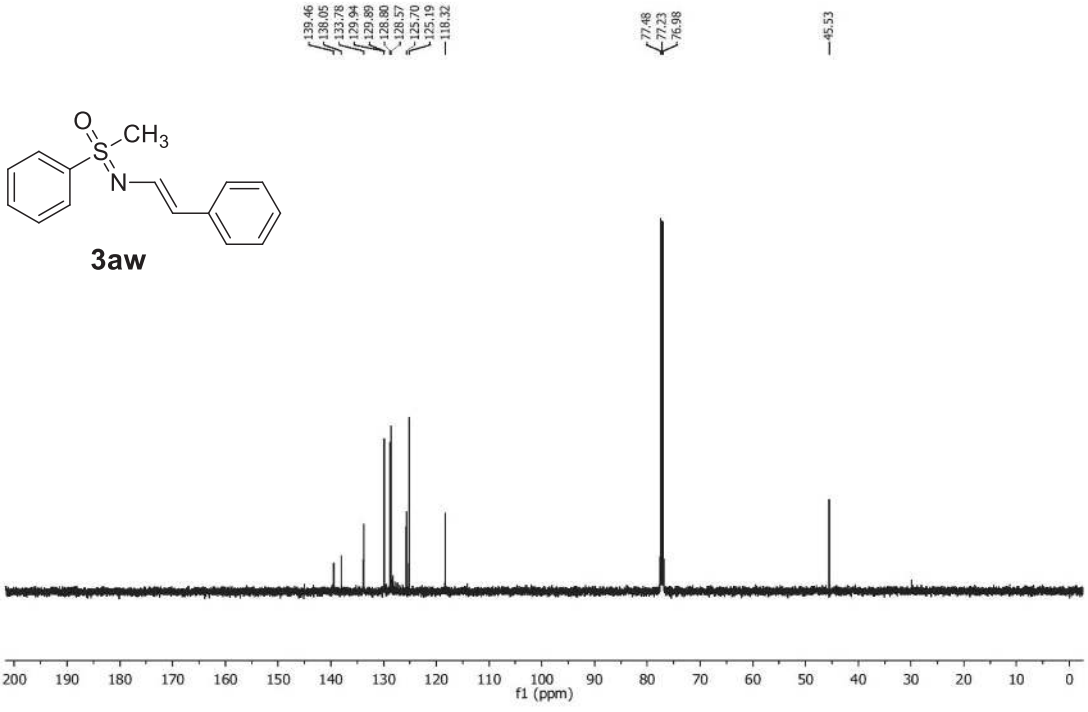


Figure 4.5 ^{13}C NMR of *N*-phenylethynyl-*S,S*-methylphenylsulfoximine (**3aw**)

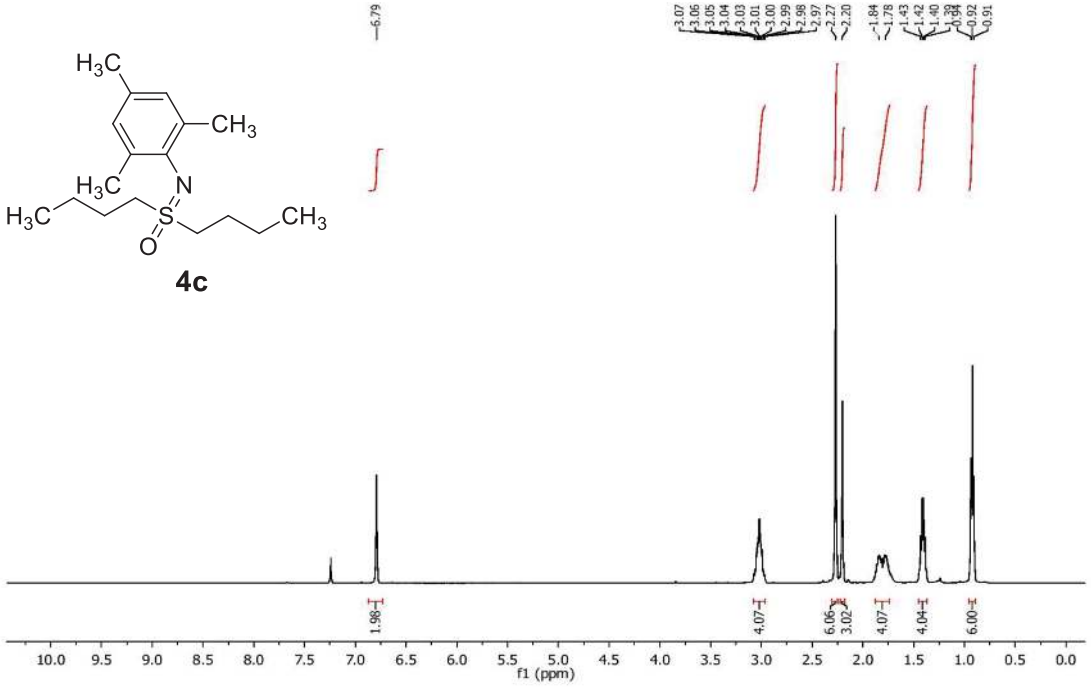


Figure 4.6 ^{1}H NMR of *N*-(2,4,6-trimethylphenyl)-*S,S*-dibutylsulfoximine (**4c**)

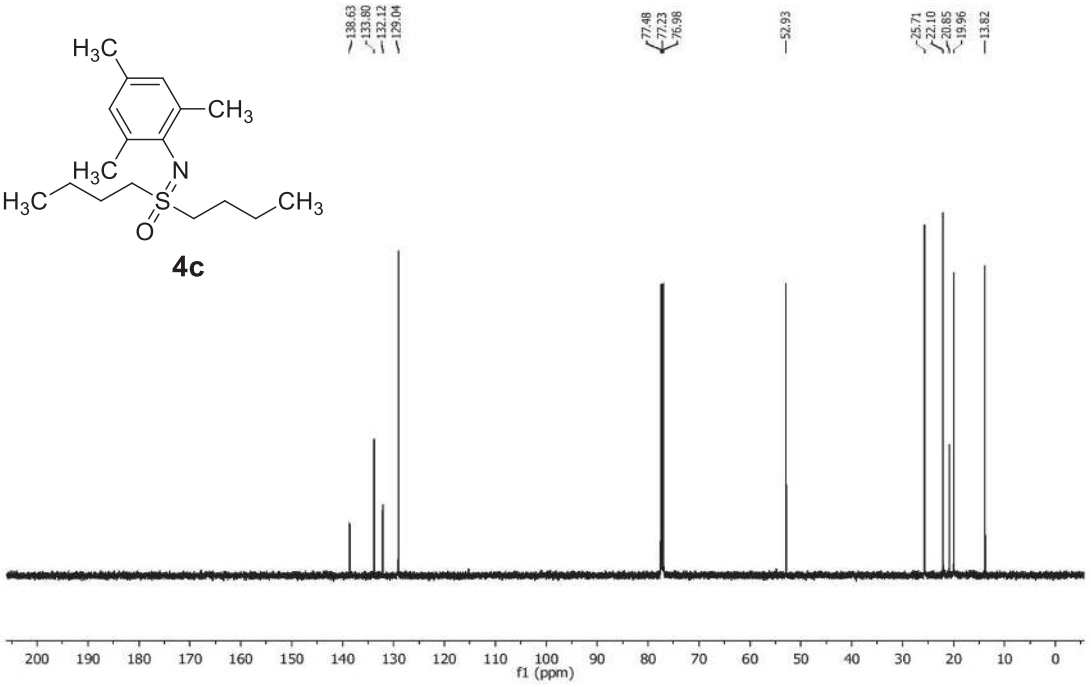


Figure 4.7 ^{13}C NMR of *N*-(2,4,6-trimethylphenyl)-*S,S*-dibutylsulfoximine (**4c**)

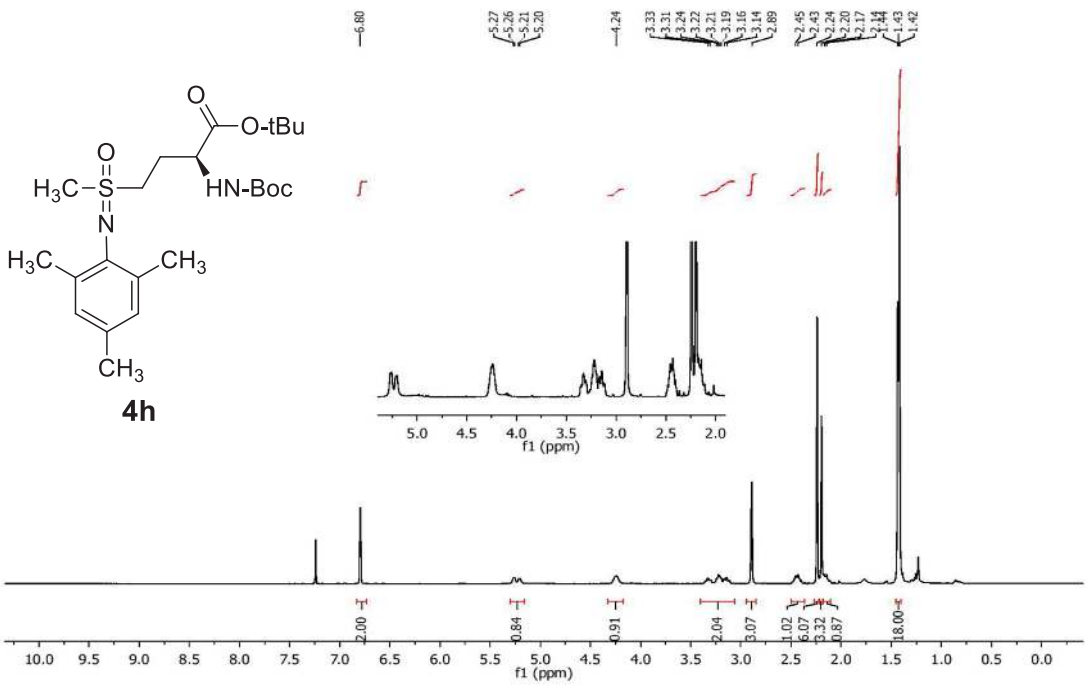


Figure 4.8 ^{1}H NMR of L-Methionine Sulfoximine Derivative (**4h**)

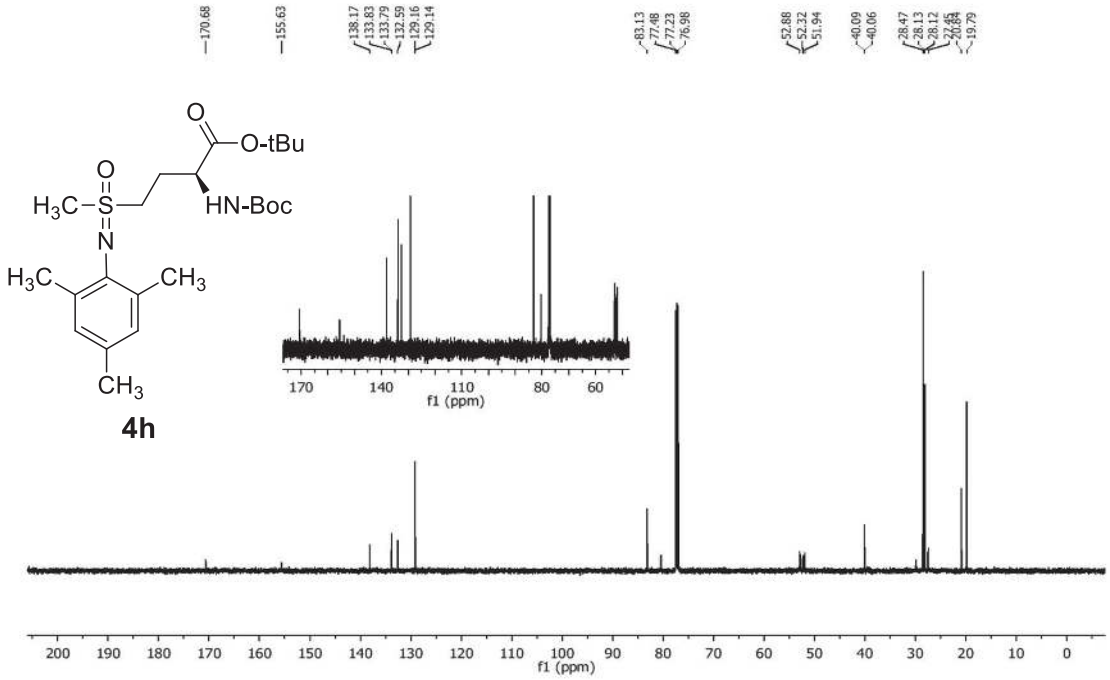


Figure 4.9 ^{13}C NMR of L-Methionine Sulfoximine Derivative (**4h**)

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