CHAPTER-5

Copper-Promoted Dehydrogenative Cross-Coupling Reaction of Dialkyl Phosphites with Sulfoximines

5.1 Introduction

Organophosphorus compounds have widespread applications in many different fields including organic synthesis, medicinal chemistry, agrochemicals, material sciences [1-5]. Among this family of compounds, phosphoramidates have received considerable interest over the past few decades due to their significance in medicinal chemistry [6-11].

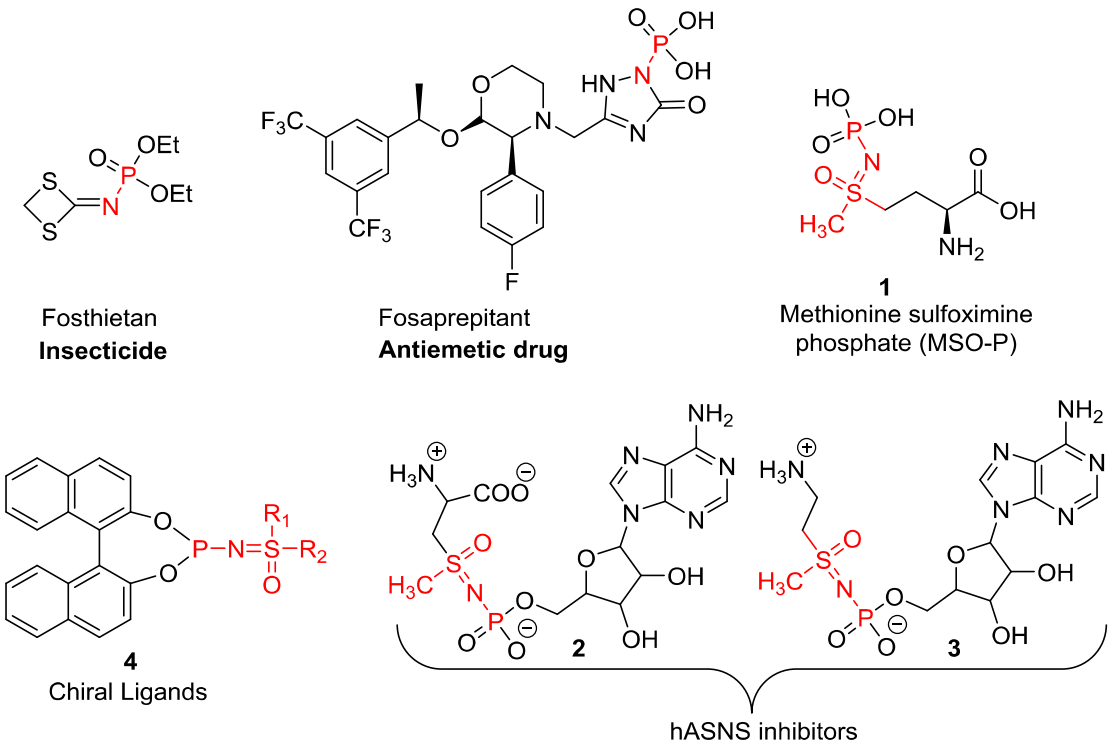
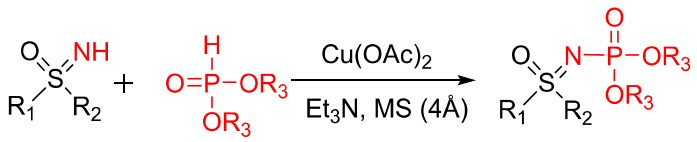


Figure 5.1: Structures of some important phosphoramidates.

For instance, phosphoramidate functionalities are found in many drugs (e.g. Fosthietan, Stampidine, Fosaprepitant and Ceftaroline Fosamil), natural products and bioactive molecules (Figure **5.1**) [1-11]. Besides, phosphoramidate compounds have been employed as organocatalysts in asymmetric synthesis [12, 13]. Sulfoximines have been explored as building blocks, organocatalysts, ligands, chiral auxiliaries, directing groups, etc. in synthetic organic chemistry [14-27]. Moreover, molecules with sulfoximine motifs have gained significant attention in drug discovery [28-31]. In this context, sulfoximine-derived

phosphoramidates are also known in the literature for their important roles in biology (Figure **5.1, 1-4**) [32-36]. For instance, methionine sulfoximine phosphate (MSO-P, 1) is the active form of methionine sulfoximine (MSO) which inhibits glutamine synthetase efficiently [32]. Sulfoximine-derived phosphoramidates (**2**) and (**3**) were found to be potent inhibitors of human asparagine synthetase (hASNS) with nano-molar concentrations [33-35]. On the other hand, *N*-phosphino sulfoximines have been successfully used as chiral ligands for different asymmetric catalysis reactions [37-40]. For example, Bolm's research group has explored BINOL-derived *N*-phosphino sulfoximines (**4**) as efficient chiral ligands for the Rh-catalyzed asymmetric hydrogenation of functionalized olefins [39]. Phosphoramidates are typically prepared by the reaction of amines with halophosphates in the presence of base [41]. However, the difficulty of preparation and handling of hazardous phosphoryl halides poses a need for a more acceptable alternative. In this context, dehydrogenative cross-coupling of dialkyl phosphites with different amines received significant attention recently [42-44]. Despite their importance, it is surprising that the synthesis of sulfoximine derived phosphoramidates is not yet well explored in organic synthesis [36, 42]. Licastro *et al.* reported the classical synthesis of some *N*-phosphorylated sulfoximines using chloroethylphosphates in the presence of triethylamine [36]. Later, Prabhu *et al.* reported the molecular iodine-hydrogen peroxide mediated coupling of sulfoximine with different dialkyl phosphites through the halophosphate intermediate (Only one example of sulfoximine was investigated) [42]. Although this method was found to be very efficient with different types of amines, low yields were observed in the case of sulfoximine. It is probably due to the poor nucleophilicity of sulfoximines. It is also worthwhile to mention that so far there is no direct dehydrogenative coupling of dialkyl phosphites with sulfoximines reported. Therefore, we

believe that there is still room for the development of better procedures to achieve sulfoximine derived phosphoramidates in good yields under mild conditions. Copper is an indispensable metal in organic synthesis explored in many cross-coupling reactions including *Chan-Lam* reactions and *Ullman* condensation reactions [45-46]. Moreover, recently a copper-prompted *N*-phosphorylation of different amines and amides was reported with different dialkyl phosphites [43, 44]. It is also noteworthy that copper played an important role in different *N*-functionalization reactions of sulfoximines [47-51]. In continuation of our previous chapter works [52-54], here we disclose copper(II) acetate mediated *N*-phosphorylation of sulfoximines with different dialkyl phosphites under mild reaction conditions (Scheme **5.1**).



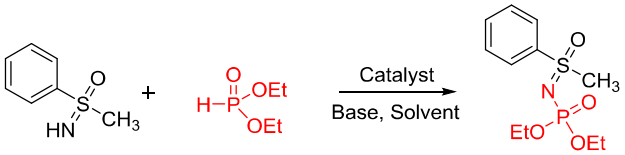
Scheme 5.1: Dehydrogenative coupling of dialkyl phosphites with sulfoximines.

5.2 Results and Discussion

At the outset, the optimization of N-P bond formation between *S,S*-methylphenylsulfoximine (**1a**) and diethyl phosphite (**2a**) was investigated in acetonitrile using 10 mol% of various copper(I) and copper(II) salts at 50 °C. The reactions were carried out in the absence of base and additives under open air condition (Table **5.1**, entries **1-8**). Most of the copper salts failed to provide the desired product even after 12 h while copper(II) acetate gave the desired product **3aa** in a trace amount. Increasing the reaction temperature to 80 °C gave only a slight improvement in the yield of the desired product, i.e. only 9% (Table **5.1**, entry **9**). Hence, the reaction condition was further optimized in the presence of different organic bases

such as pyridine, 4-Dimethylaminopyridine (4-DMAP) and triethylamine; inorganic bases such as cesium carbonate, potassium carbonate and potassium phosphate respectively, with copper(II) acetate at 80 °C (Table **5.1**, entries **10-15**). Among them, triethylamine was found to be most suitable, providing the desired product 3aa in 20% yield in acetonitrile (Table **5.1**, entry **12**). Encouraged, the reaction was further carried out in different solvents including 1,2-DCE, 1,4-dioxane, toluene and tetrahydrofuran (THF) with copper(II) acetate in the presence of triethylamine at 80 °C (Table **5.1**, entries **16-19**). Among these solvents, toluene was identified as an efficient solvent which afforded the desired product in 29% yield (Table **5.1**, entries **18**). Seeking to further optimize the conditions, the reactions were performed with increased amount of copper(II) acetate (i.e. 20-50 mol%) (Table **5.1**, entries **20** and **21**) and elevated temperature (i.e. 80-110 °C) in toluene (Table **5.1**, entries **21–23**).

Table 5.1: Optimization of the reaction condition.[a,b]



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

S.No.	Metal Salt	Mol%	Solvent	Base	Temperature (°C)	Time (h)	Yield (%)[b]
1	CuCl	10	CH_3CN	-	50	12	n.r
2	CuI	10	CH_3CN	-	50	12	n.r
3	CuOAc	10	CH_3CN	-	50	12	n.r
4	Cu_2O	10	CH_3CN	-	50	12	n.r
5	$Cu(OAc)_2$	10	CH_3CN	-	50	12	~5
6	$CuCl_2$	10	CH_3CN	-	50	12	n.r
7	$CuBr_2$	10	CH_3CN	-	50	12	n.r
8	$CuSO_4$	10	CH_3CN	-	50	12	n.r
9	$Cu(OAc)_2$	10	CH_3CN	-	80	12	9
10	$Cu(OAc)_2$	10	CH_3CN	Pyridine	80	12	16
11	$Cu(OAc)_2$	10	CH_3CN	4-DMAP	80	12	12
12	$Cu(OAc)_2$	10	CH_3CN	Et_3N	80	12	20

13	$Cu(OAc)_2$	10	CH_3CN	Cs_2CO_3	80	12	10
14	$Cu(OAc)_2$	10	CH_3CN	K_2CO_3	80	12	15
15	$Cu(OAc)_2$	10	CH_3CN	K_3PO_4	80	12	13
16	$Cu(OAc)_2$	10	DCE	Et_3N	80	12	n.r
17	$Cu(OAc)_2$	10	Dioxane	Et_3N	80	12	n.r
18	$Cu(OAc)_2$	10	Toluene	Et_3N	80	12	29
19	$Cu(OAc)_2$	10	THF	Et_3N	80	12	n.r
20	$Cu(OAc)_2$	20	Toluene	Et_3N	80	12	35
21	$Cu(OAc)_2$	30	Toluene	Et_3N	80	12	47
22	$Cu(OAc)_2$	50	Toluene	Et_3N	80	12	50
23	$Cu(OAc)_2$	30	Toluene	Et_3N	110	12	78
24	**$Cu(OAc)_2$**	**30**	**Toluene**	**Et_3N**	**110**	**4**	**89[c]**
25	$Cu(OAc)_2$	30	Toluene	Et_3N	110	4	~ 5[d]
26	$NiCl_2$	30	Toluene	Et_3N	110	4	n.r[c]
27	$Ni(OAc)_2$	30	Toluene	Et_3N	110	4	n.r[c]
28	$FeCl_3$	30	Toluene	Et_3N	110	4	n.r[c]
29	$Pd(OAc)_2$	30	Toluene	Et_3N	110	4	n.r[c]

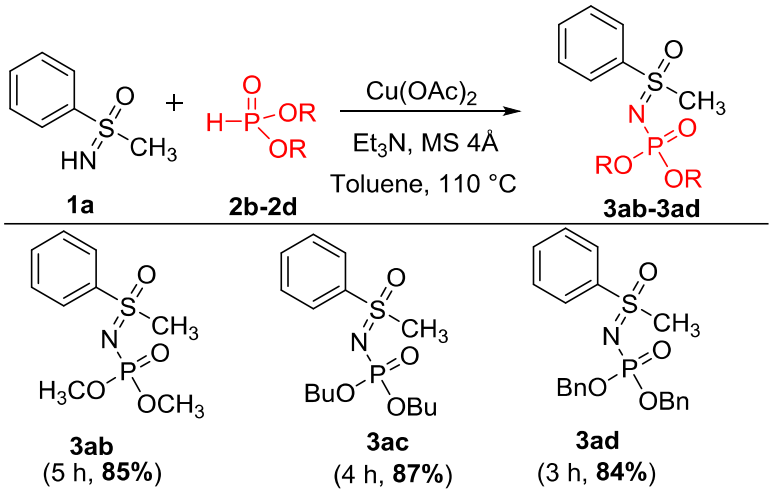
[a]Reaction condition: Sulfoximine (155 mg, 1 mmol), diethylphosphite (276 mg, 2 eq.), catalyst, base (1 eq.), solvent (8 mL). [b]Isolated yield. [c]Reaction carried out with 4Å molecular sieves. [d]Rection was performed in the presence of 0.2 mL H_2O.

To our delight, the desired product was obtained in 78% yield after 12 h in the presence of 30 mol% of copper(II) acetate at 110 °C (Table **5.1**, entry **23**). It is important to mention that the addition of 4Å molecular sieves in the reaction mixture noticeably increased the product yield to 89% within 4 hours (Table **5.1**, entry **24**). We believe that the molecular sieves help to maintain the anhydrous condition in the reaction medium and enhance the rate of the reaction significantly. To understand this, the desired reaction was performed in the presence of 200 µL water (Table **5.1**, entry **25**). As expected, the reaction provided the desired coupling product only in negligible amount. It is also worth noting that the other metal catalysts such as nickel(II) chloride, nickel(II) acetate, iron(III) chloride and palladium(II) acetate failed to provide the desired product (Table **5.1**, entries **26-29**).

5.3 Substrates Scope

After finding the optimized condition, we explored the scope of different dialkyl phosphites (**2b-d**) in the coupling reaction with *S,S*-methylphenylsulfoximine (**1a**). To our delight, dimethyl, dibutyl and dibenzyl phosphites participated in the coupling reaction very efficiently and provided the desired products **3ab-3ad** in 84-87% yields within the period of 3-5 hrs (Table **5.2**).Encouraged, we further investigated the dehydrogenative cross-coupling reaction of diethyl and dibutyl phosphites with different sulfoximines (Table **5.3**). *S*-Phenylsulfoximines bearing linear and branched alkyl chains underwent *N*-phosphorylation with both diethyl and dibutyl phosphites in excellent yields (Table **5.3**, **3ba-3ea** and **3bc-3ec**). It is worth noting that sterically encumbered *S,S-iso*-propylphenylsulfoximine also furnished the desired products in high yields (Table **5.3**, **3ea** and **3ec**).

Table 5.2: *N*-Phosphorylation of sulfoximine with different dialkyl phosphites.[a,b]

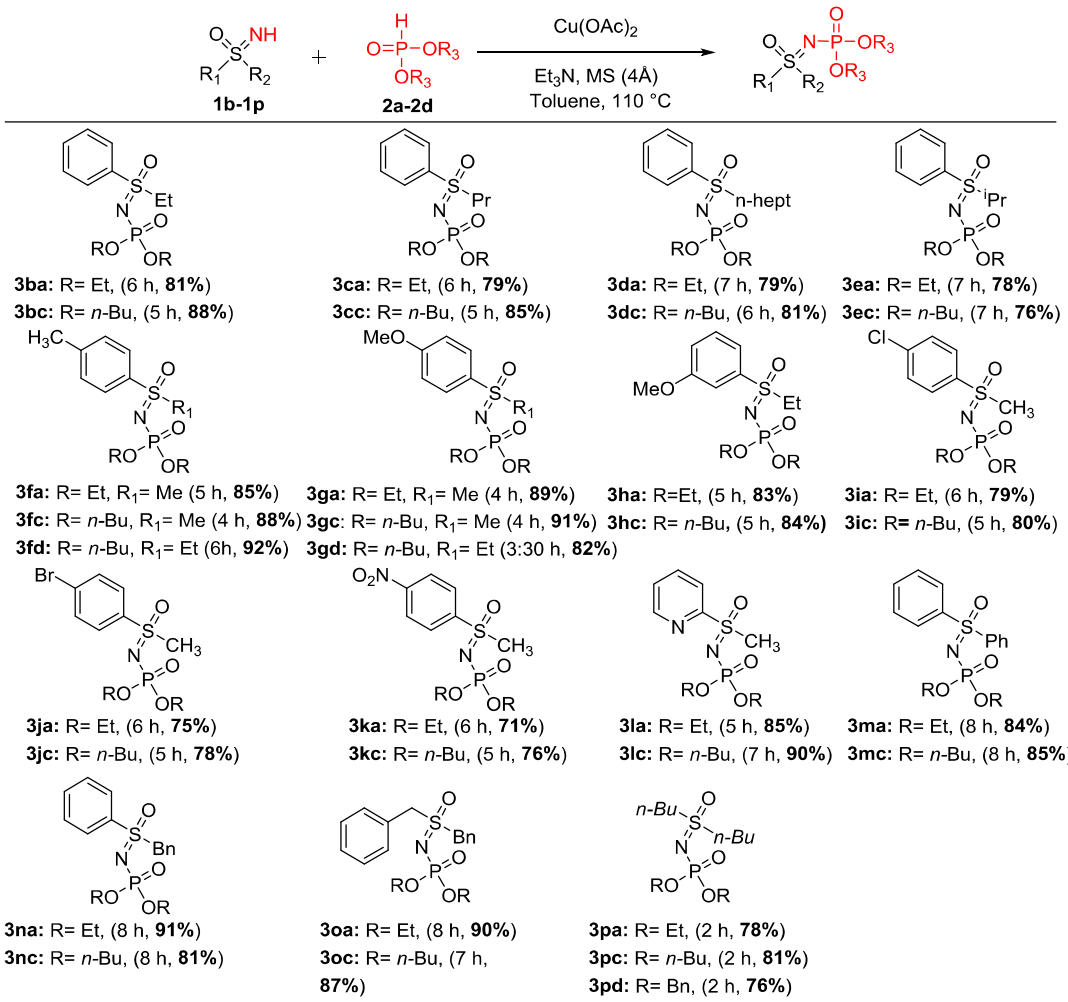


[a]Sulfoximine (0.5 mmol), dialkyl/dibenzyl phosphite (2 eq.), $Cu(OAc)_2$ (0.3 eq.), triethylamine (1 eq.), MS (4Å), toluene (5 mL). [b]Isolated yield.

Further, *N*-phosphorylation of sulfoximines bearing different substitutions on the aryl ring (*i.e.* methyl, methoxy, chloro, bromo and nitro groups) were investigated (Table **5.3**, **3fa-3ka** and **3fc-3kc**). In fact, the effect of electron donating and withdrawing groups present on the aryl ring was found to be minimal in the *N*-phosphorylation process. All these

substrates underwent coupling with diethyl and dibutyl phosphites in good to excellent yields within the period of 5-6 hours. Interestingly, heterocyclic sulfoximine also participated in the coupling reaction smoothly and gave the desired products **3la** and **3lc** in 85-90% yields.

Table 5.3: *N*-Phosphorylation of various sulfoximines with diethyl and dibutyl phosphite.[a,b]



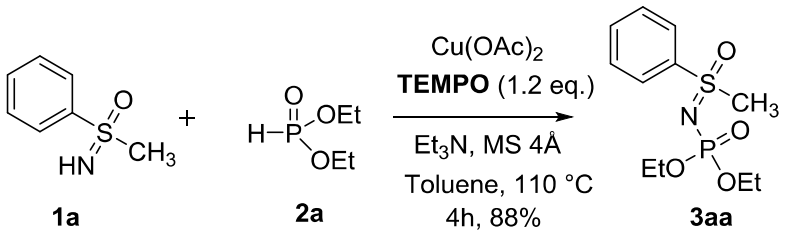
[a]Reaction condition: Sulfoximine (0.5 mmol), diethyl, dibutyl or dibenzyl phosphite (2 eq.), $Cu(OAc)_2$ (0.3 eq.), triethylamine (1 eq.), MS (4Å), toluene (5 mL). [b]isolated yield.

The substrate scope was further elaborated by subjecting aryl-aryl, aryl-benzyl and benzyl-benzyl sulfoximines with diethyl and dibutyl phosphite under optimized condition. These reactions proceeded well and provided the desired products in 84-91% yields (Table **5.3**,

3ma-3oa and **3mc-3oc**). Furthermore, alkyl sulfoximine also participated in the coupling reaction efficiently with various dialkyl phosphites under optimized condition (Table **5.3**, **3pa**, **3pc** and **3pd**). In fact, dialkyl sulfoximines require relatively less time for the coupling reaction when compared with aryl sulfoximines. Overall, the developed methodology was found to be more convenient and suitable for the preparation of sulfoximine-derived phosphoramidates in good yields.

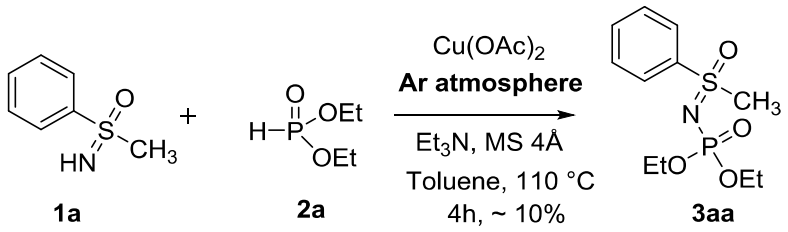
5.4 Plausible reaction mechanism

To understand the mechanism of the reaction, few controlled experiments were performed. Initially, the reaction was performed in the presence of radical scavenger 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) under optimized condition (Scheme **5.2**). The reaction proceeded smoothly and gave the desired product in 88% yield suggesting that the reaction does not proceed through a radical mechanism.

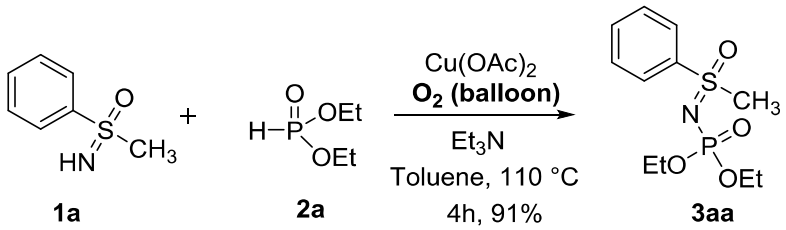


Scheme 5.2: Coupling reaction in the presence of radical scavenger TEMPO.

Further, to investigate the role of oxygen/air, the reactions were performed under argon as well as oxygen atmosphere (Scheme **5.3** and **5.4**). Under the inert condition, the reaction yielded the desired product in very low yield (~ 10%) while 91% was obtained in the presence of oxygen.

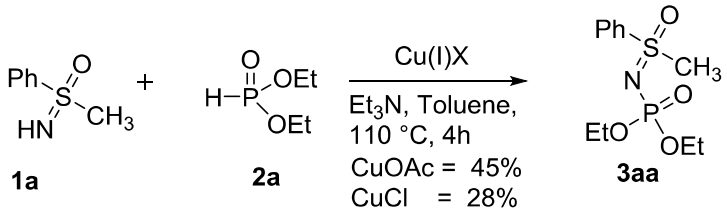


Scheme 5.3: Coupling reaction under inert condition.



Scheme 5.4: Coupling reaction under oxygen atmosphere.

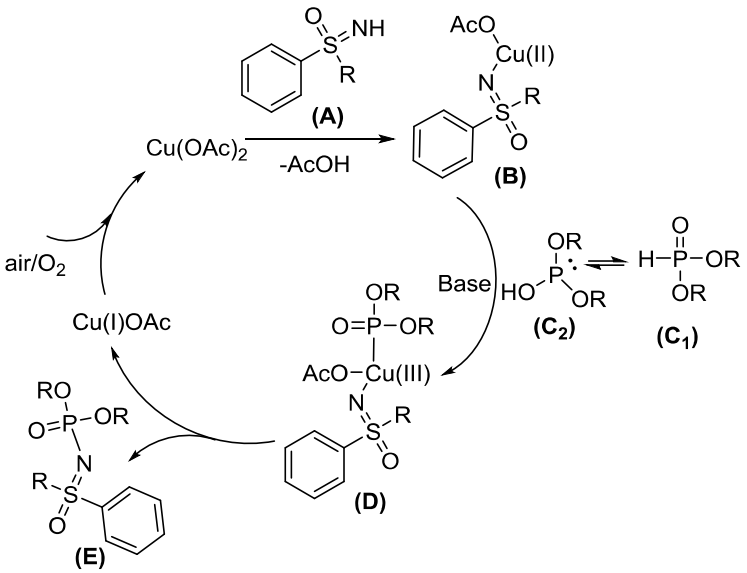
This clearly indicates the involvement of oxygen in the catalytic cycle. It is also known that often Cu(II) is disproportionate to form Cu(I) which also involved in the catalytic cycle. To understand this, the reaction was also performed with copper(I) salts instead of $Cu(OAc)_2$ (Scheme **5.5**). It was observed that copper(I) acetate provided 45% of the desired product while 28% was obtained with copper(I) chloride. These results indicate that copper(I) intermediate might also participate in the coupling reaction.



Scheme 5.5: Coupling reaction with copper(I) salts.

Based on these observations and literature reports [43-44], a plausible mechanism has been proposed as shown in Scheme **5.6**. At the beginning, copper(II) acetate undergoes ligand exchange reaction with sulfoximine **A** to generate the intermediate **B**. Further, the

phosphite intermediate **C** undergoes an addition reaction with intermediate **B** to form copper(III) complex **D** in the presence of base. The complex **D** undergoes reductive elimination to provide the desired product **E** and Cu(I) intermediate. Finally, Cu(I) is oxidized to copper(II) in the presence of air/oxygen.



Scheme 5.6: Plausible Mechanism of the Reaction.

5.5 Conclusions

In conclusion, an efficient methodology has been demonstrated for the synthesis of *N*-phosphorylated sulfoximine under mild conditions. A library of sulfoximines underwent coupling reaction with dialkyl phosphites in the presence of copper(II) acetate and provided the desired products in good to excellent yields. Notably, heteroaromatic sulfoximine as well as dialkyl sulfoximines also participated in coupling reaction smoothly and gave the desired products in excellent yields. We anticipate that the current practical methodology will be highly useful for the synthesis of *N*-phosphorylated sulfoximines.

5.6 Experimental Section

5.6.1 Experimental procedure for the optimization table

A mixture of *S,S*-methylphenylsulfoximine (155 mg, 1 mmol) and metal salt (appropriate amount) was stirred in a different solvent (5 mL) at room temperature for 5 minutes under open air condition. Round-bottom flask containing reaction mixture was transferred to pre-heated oil bath and stirred for 5 minutes at appropriate temperature to which diethyl phosphite (276 mg, in 3 mL of appropriate solvent) was added in the presence of or absence of molecular sieves (300 mg) and base (1 eq.). The progress of the reaction was seen by thin layer chromatography using ethyl acetate (EA)/hexane as an eluent. After completion of the reaction (or appropriate time), the reaction mixture was diluted with DCM and washed with water and brine solution. The reaction mixture was dried over anhydrous sodium sulfate and evaporated. The crude product was purified on silica-gel (100-200 mesh) column chromatography using ethyl acetate/hexane as an eluent to obtain **3aa**. R_f (100% EA) 0.22.

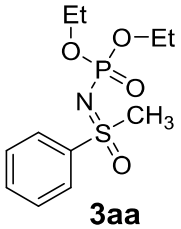
5.6.2 Experimental procedure for the synthesis of sulfoximine derived phosphoramidates with dialkyl phosphites

Sulfoximine (0.5 mmol, 1 eq.), copper(II) acetate (0.5 eq.), triethylamine (1 eq.) and toluene (3 mL) were added in round-bottom flask containing pre-activated molecular sieve (150 mg) and stirred at room temperature for 5 minutes under open air condition. Round-bottom flask containing reaction mixture was transferred to pre-heated oil bath. In another round-bottom flask, dialkyl phosphite (1.0 mmol, 2 eq.) was diluted with 2 mL toluene. The diluted dialkyl phosphite was added into the reaction mixture in 3 to 4 part for 10 minutes of time interval and kept for vigorous stirring at 110 $^{\circ}$C. The RB flask was equipped with an air condenser. It is worth noting that while adding diluted dialkyl phosphite the color of reaction mixture changes from dark blue to pale blue and this color persists after consumption of the starting

material. The progress of the reaction was monitored by thin layer chromatography using ethyl acetate/hexane as an eluent. After completion of the reaction, reaction mixture was diluted with dichloromethane and washed with water and brine solution. The reaction mixture was treated with anhydrous sodium sulfate and dried in rota evaporator. The crude product was further purified on silica-gel (100–200 mesh) column chromatography using ethyl acetate/hexane as an eluent.

5.7 Analytical data for *N*-(dialkylphosphite)sulfoximines

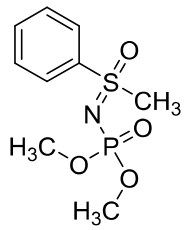
5.7.1 Diethyl (*S*-methylsulfonimidoyl)benzene phosphoroamidate (3aa):



3aa

The reaction was carried out using 155 mg of sulfoximine according to general procedure. The title compound was obtained as transparent oil, 258 mg, 89% yield. The residue was isolated by silica-gel Column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (100% EA) 0.22. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.03 (d, J = 7.5 Hz, 2H), 7.63 (dt, J = 15.4, 7.4 Hz, 3H), 4.14–4.04 (m, 4H), 3.35 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H), 1.26 (t, J = 7.1 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 140.6 (d, J = 9.0 Hz), 133.9, 129.5, 127.4, 62.8 (dd, $J_{C\text{-}P}$ = 6.0, 3.7 Hz), 46.9 (d, J = 3.3 Hz), 16.2 (dd, $J_{C\text{-}P}$ = 7.5, 4.3 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.94. **HRMS** (ESI-TOF) calcd. for $C_{11}H_{19}NO_4PS$ $[M + H]^+$ 292.0772; found 292.0759.

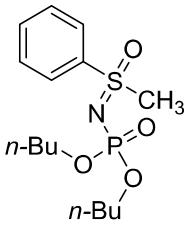
5.7.2 Dimethyl (*S*-methylsulfonimidoyl)benzene phosphoroamidate (3ab):



3ab

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 112 mg, 85% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.22. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.02 (d, J = 7.3 Hz, 2H), 7.68 (d, J = 6.9 Hz, 1H), 7.61 (d, J = 7.2 Hz, 2H), 3.74 (m, 6H), 3.36 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 140.4 (d, J = 9.2 Hz), 134.0, 129.6, 127.3, 53.6 (dd, $J_{C\text{-}P}$ = 6.2, 2.6 Hz), 46.9 (d, J = 3.0 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ 0.75. **HRMS** (ESI-TOF) calcd. for $C_9H_{15}NO_4PS$ $[M + H]^+$ 264.0459; found 264.0447.

5.7.3 Dibutyl (*S*-methylsulfonimidoyl)benzene phosphoroamidate (3ac):

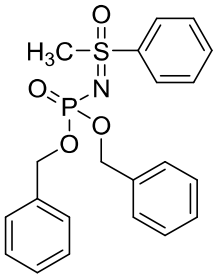


3ac

The reaction was carried out using general procedure. The title compound was obtained as pale yellow oil, 150 mg, 87% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.24. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.00 (dd, J = 7.7, 6.6 Hz, 2H), 7.65 (t, J = 7.4 Hz, 1H), 7.57 (t, J = 7.7 Hz, 2H), 4.00 (dq, J = 23.8, 6.7 Hz, 4H), 3.33 (s, 3H), 1.65–1.56 (m, 4H), 1.36 (ddd, J = 25.8, 15.0, 7.5 Hz, 4H), 0.88 (dt, J = 13.4, 7.4 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 140.6 (d, J = 8.7 Hz), 133.8, 129.5, 127.4, 66.5 (dd, $J_{C\text{-}P}$ = 6.4, 1.0 Hz), 45.9 (d, J = 3.5 Hz), 32.4 (dd, $J_{C\text{-}P}$ = 7.5, 3.4 Hz), 18.8 (d, J = 5.6 Hz), 13.7 (d, J = 2.9 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.77 (p, J = 6.7 Hz). **HRMS** (ESI-TOF) calcd. for

$C_{15}H_{27}NO_4PS$ $[M + H]^+$ 348.1398; found 348.1379.

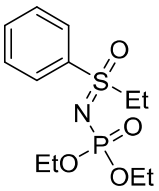
5.7.4 Dibenzyl (*S*-methylsulfonimidoyl)benzene phosphoroamidate (3ad):



3ad

The reaction was carried out using general procedure. The title compound was obtained as pale yellow liquid, 174 mg, 84% yield. The product was isolated by silica-gel column chromatography using 50% ethyl acetate:hexane as an eluent. R_f (80% ethyl acetate) = 0.24. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.88 (d, J = 7.5 Hz, 2H), 7.59 (t, J = 7.3 Hz, 1H), 7.48 (t, J = 7.3 Hz, 2H), 7.33–7.29 (m, 10H), 5.03–4.97 (m, 4H), 3.26 (s, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 140.3 (d, J = 8.9), 136.7 (dd, $J_{C\text{-}P}$ = 7.7, 3.2 Hz),133.9, 129.5, 128.4, 128.1 (d, J = 3.0 Hz), 127.8 (d, J = 16.3 Hz), 127.3, 68.3 (d, $J_{C\text{-}P}$ = 5.8 Hz), 46.9 (d, J = 3.5 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.83. **HRMS** (ESI-TOF) calcd. for $C_{21}H_{23}NO_4PS$ $[M+H]^+$: 416.1085, found 416.1071.

5.7.5 Diethyl (*S*-ethylsulfonimidoyl)benzene phosphoroamidate (3ba):

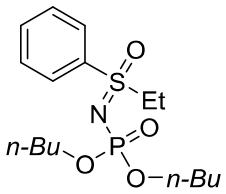


3ba

The reaction was carried out using general procedure. The title compound was obtained as transparent liquid, 123 mg, 81% yield. The product was isolated by silica-gel column chromatography using 50% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.22. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.93 (d, J = 7.7 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.7 Hz, 2H), 4.08–3.97 (m, 4H), 3.42 (dt, J = 14.8, 7.3 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H), 1.19 (td, J = 7.1, 2.8 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 137.80 (d, J = 7.5 Hz), 133.8, 129.3, 128.2, 62.63 (dd, $J_{C\text{-}P}$ = 6.0, 3.5 Hz), 52.90 (d, J = 4.5

Hz), 16.14 (t, J_{C-P} = 7.1 Hz), 7.9; **^{31}P NMR (200 MHz, CDCl$_3$)** δ -1.77 (p, J =7.2 Hz). **HRMS** (ESI-TOF) calcd. for $C_{12}H_{21}NO_4PS$ [M + H]$^+$ 306.0929; found 306.0910.

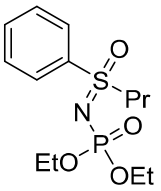
5.7.6 Dibutyl (*S*-ethylsulfonimidoyl)benzene phosphoroamidate (3bc):



3bc

The reaction was carried out using general procedure. The title compound was obtained as transparent liquid, 158 mg, 88% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.24. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 7.96–7.94 (m, 2H), 7.65–7.62 (m, 1H), 7.57–7.54 (m, 2H), 3.99 (qd, J = 6.7, 1.1 Hz, 2H), 3.93 (q, J = 6.7 Hz, 2H), 3.44–3.38 (m, 2H), 1.64–1.58 (m, 2H), 1.55–1.49 (m, 2H), 1.38–1.34 (m, 2H), 1.29 (dd, J = 7.4, 5.8 Hz, 2H), 1.21 (t, J = 7.4 Hz, 3H), 0.87 (t, J = 7.4 Hz, 3H), 0.83 (t, J = 7.4 Hz, 3H); **^{13}C NMR (125 MHz, CDCl$_3$)** δ 138.0 (d, J = 7.2 Hz), 133.7, 129.3, 128.3, 66.4 (dd, J_{C-P} = 6.4, 4.7 Hz), 52.9 (d, J = 4.7 Hz), 32.3 (dd, J_{C-P} = 7.5, 6.2 Hz), 18.8 (d, J = 8.5 Hz), 13.7 (d, J = 4.3 Hz), 7.9; **^{31}P NMR (200 MHz, CDCl$_3$)** δ -1.62 (p, J =6.9 Hz). **HRMS** (ESI-TOF) calcd. for $C_{16}H_{29}NO_4PS$ [M + H]$^+$ 362.1555; found 362.1544.

5.7.7 Diethyl (*S*-propylsulfonimidoyl)benzene phosphoroamidate (3ca):

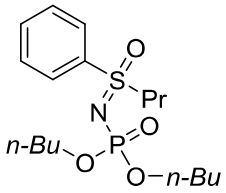


3ca

The reaction was carried out using general procedure. The title compound was obtained as pale yellow liquid, 126 mg, 79% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (80% ethyl acetate) = 0.20.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, J = 8.1 Hz, 2H), 7.66 (t, J = 7.4 Hz, 1H), 7.57 (t, J = 7.7 Hz, 2H), 4.12–4.0 (m, 4H), 3.44–3.35 (m, 2H), 1.70–1.66 (m, 2H), 1.31 (t, J = 7.1 Hz, 3H), 1.23 (d, J = 7.4 Hz, 3H), 0.94 (t, J = 7.4 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 138.6 (d, J = 7.4 Hz), 133.8, 129.4, 128.2, 62.8–62.5 (m), 60.07 (d, J = 4.4 Hz), 17.0, 16.4–16.1 (m), 12.5; **^{31}P NMR** (200 MHz, $CDCl_3$) δ -1.82. **HRMS** (ESI-TOF) calcd. for $C_{13}H_{23}NO_4PS$ $[M + H]^+$ 320.1085; found 320.1071.

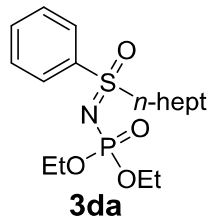
5.7.8 Dibutyl (*S*-propylsulfonimidoyl)benzene phosphoroamidate (3cc):



3cc

The reaction was carried out using general procedure. The title compound was obtained as pale yellow oil, 160 mg, 85% yield. The product was isolated by silica-gel column chromatography using 80% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.22. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.96 (dd, J = 7.4, 0.9 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.56 (t, J = 7.0 Hz, 2H), 3.97 (ddd, J = 18.6, 12.5, 5.2 Hz, 4H), 3.40–3.32 (m, 2H), 1.65–1.61 (m, 4H), 1.53–1.51 (m, 2H), 1.38 (dd, J = 13.6, 7.3 Hz, 2H), 1.29 (dd, J = 15.2, 7.8 Hz, 2H), 0.91 (dt, J = 15.1, 7.4 Hz, 6H), 0.85 (t, J = 7.4 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 138.7 (d, J = 7.1 Hz), 133.7, 129.4, 128.2, 66.4 (t, $J_{C\text{-}P}$ = 6.0 Hz), 60.0 (d, J = 4.6 Hz), 32.3 (t, $J_{C\text{-}P}$ = 7.4 Hz), 18.8 (t, J = 8.2 Hz), 16.9, 13.7 (t, J = 5.8 Hz), 12.7; **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.67. **HRMS** (ESI-TOF) calcd. for $C_{17}H_{31}NO_4PS$ $[M + H]^+$ 376.1711; found 376.1691.

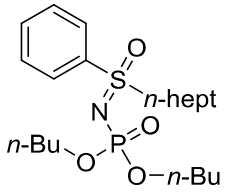
5.7.9 Diethyl (*S*-*n*-heptylsulfonimidoyl)benzene phosphoroamidate (3da):



3da

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 148 mg, 79% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.22. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.94 (d, J = 7.5 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 7.7 Hz, 2H), 4.09–3.97 (m, 4H), 3.37 (dtd, J = 13.9, 8.9, 5.9 Hz, 2H), 1.61–1.57 (m, 2H), 1.27 (t, J = 7.1 Hz, 4H), 1.24–1.14 (m, 10H), 0.79 (t, J = 7.0 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 138.5 (d, J = 7.2 Hz), 133.7, 129.3, 128.1, 62.6 (t, $J_{C\text{-}P}$ = 5.5 Hz), 58.3 (d, J = 4.5 Hz), 31.4, 28.6, 27.9, 23.0, 22.4, 16.1 (dd, $J_{C\text{-}P}$ = 9.0, 7.7 Hz), 14.0; **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.87. **HRMS** (ESI-TOF) calcd. for $C_{17}H_{31}NO_4PS$ $[M + H]^+$ 376.1711; found 376.1688.

5.7.10 Dibutyl (*S*-*n*-heptylsulfonimidoyl)benzene phosphoroamidate (3dc):

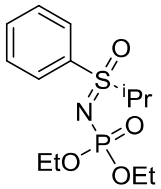


3dc

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 174 mg, 81% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.24. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.96 (d, J = 7.4 Hz, 2H), 7.64 (t, J = 7.4 Hz, 1H), 7.56 (t, J = 7.7 Hz, 2H), 4.00 (q, J = 6.7 Hz, 2H), 3.93 (q, J = 6.7 Hz, 2H), 3.41–3.38 (m, 1H), 3.34–3.32 (m, 1H), 1.61 (dd, J = 14.6, 6.9 Hz, 3H), 1.55–1.49 (m, 2H), 1.37 (dd, J = 15.0, 7.5

Hz, 2H), 1.28 (dd, J = 15.2, 7.6 Hz, 4H), 1.24–1.11 (m, 7H), 0.89 (t, J = 7.4 Hz, 3H), 0.83 (dt, J = 14.2, 7.3 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 138.7 (d, J = 6.9 Hz), 133.7, 129.3, 128.2, 66.4 (t, $J_{C\text{-}P}$ = 6.4 Hz), 58.4 (d, J = 4.6 Hz), 32.3 (t, $J_{C\text{-}P}$ = 7.8 Hz), 31.4, 28.7, 28.0, 23.0, 22.5, 18.8 (d, J = 10.5 Hz), 14.0, 13.7 (d, J = 4.9 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.63. **HRMS** (ESI-TOF) calcd. for $C_{21}H_{39}NO_4PS$ $[M + H]^+$ 432.2337; found 432.2312.

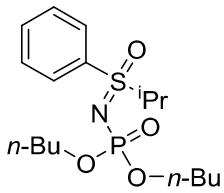
5.7.11 Diethyl (*S-iso*-propylsulfonimidoyl)benzene phosphoroamidate (3ea):



3ea

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 124 mg, 78% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.24. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.92 (d, J = 8.3 Hz, 2H), 7.66–7.61 (m, 1H), 7.55 (t, J = 7.5 Hz, 2H), 4.06–3.94 (m, 4H), 3.51 (dt, J = 13.6, 6.8 Hz, 1H), 1.26 (ddd, J = 16.9, 15.3, 6.4 Hz, 10H), 1.13 (t, J = 7.1 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 136.2 (d, J = 4.3 Hz), 133.7, 129.3, 129.1, 62.5 (dd, $J_{C\text{-}P}$ = 10.3, 6.2 Hz), 58.2 (d, J = 6.2 Hz), 16.1 (dd, $J_{C\text{-}P}$ = 15.6, 8.2 Hz), 15.7; **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.61 (p, J =7.5 Hz). **HRMS** (ESI-TOF) calcd. for $C_{13}H_{22}NO_4PS$ $[M + H]^+$ 320.1085; found 320.1089.

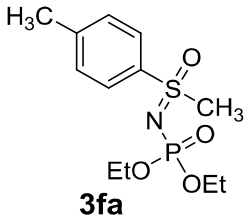
5.7.12 Dibutyl (*S-iso*-propylsulfonimidoyl)benzene phosphoroamidate (3ec):



3ec

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 142 mg, 76% yield. The product was isolated by silica-gel column chromatography using 50% ethyl acetate:hexane as an eluent. R_f (80% ethyl acetate) = 0.25. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.93–7.91 (m, 2H), 7.63 (dd, J = 10.9, 3.9 Hz, 1H), 7.54 (t, J = 7.8 Hz, 2H), 3.97 (qd, J = 6.6, 2.2 Hz, 2H), 3.88 (q, J = 6.7 Hz, 2H), 3.49 (dt, J = 13.5, 6.8 Hz, 1H), 1.59–1.58 (m, 2H), 1.44 (dd, J = 8.4, 6.7 Hz, 2H), 1.35 (dd, J = 15.0, 7.5 Hz, 2H), 1.30 (d, J = 6.8 Hz, 3H), 1.29–1.19 (m, 5H), 0.87 (dd, J = 7.7, 7.1 Hz, 3H), 0.79 (t, J = 7.4 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 136.4(d, J = 4.0 Hz), 133.6, 129.3, 129.0, 66.2(dd, $J_{C\text{-}P}$ = 16.4, 6.5 Hz), 58.2(d, J = 6.5 Hz), 32.3(dd, $J_{C\text{-}P}$ = 12.2, 7.6 Hz), 18.7(d, J = 16.1 Hz), 16.0, 15.6, 13.7(d, J = 7.6 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.39 (p, J =6.6 Hz). **HRMS** (ESI-TOF) calcd. for $C_{17}H_{31}NO_4PS$ $[M + H]^+$ 376.1711; found 376.1698.

5.7.13 Diethyl (*S*-methylsulfonimidoyl)-4-methylbenzene phosphoroamidate (3fa):

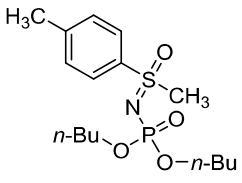


3fa

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 130 mg, 85% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.22. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.83 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 4.07–3.99 (m, 4H), 3.27 (s, 3H), 2.39 (s, 3H), 1.26 (t, J = 7.2 Hz, 3H), 1.22 (t, J = 7.0 Hz, 3H); **^{13}C NMR (125**

MHz, $CDCl_3$) δ 144.8, 137.4 (d, J = 8.8 Hz), 130.0, 127.2, 62.6 (d, $J_{C\text{-}P}$ = 5.5 Hz), 46.9 (d, J = 3.1 Hz), 21.5, 16.1 (dd, $J_{C\text{-}P}$ = 7.4, 2.4 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.88. **HRMS** (ESI-TOF) calcd. for $C_{12}H_{21}NO_4PS$ $[M + H]^+$ 306.0929; found 306.0909.

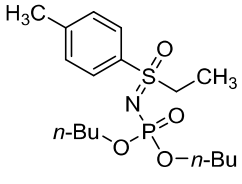
5.7.14 Dibutyl (*S*-methylsulfonimidoyl)-4-methylbenzene phosphoroamidate (3fc):



3fc

The reaction was carried out using general procedure. The title compound was obtained as transparent liquid, 158 mg, 88% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (80% ethyl acetate) = 0.24. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.88 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H), 3.99 (dq, J = 22.9, 6.7 Hz, 4H), 3.30 (s, 3H), 2.43 (s, 3H), 1.64 (dd, J = 14.3, 7.4 Hz, 2H), 1.57 (dd, J = 14.8, 6.8 Hz, 2H), 1.40–1.32 (m, 4H), 0.88 (dt, J = 12.7, 7.4 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 144.8, 137.6 (d, J = 8.8 Hz), 130.0, 127.4, 66.5 (d, $J_{C\text{-}P}$ = 6.4 Hz), 47.0 (d, J = 3.5 Hz), 32.4 (dd, $J_{C\text{-}P}$ = 7.6, 3.0 Hz), 21.6, 18.8 (d, J = 5.3 Hz), 13.7 (d, J = 2.5 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.73 (p, J =6.1 Hz). **HRMS** (ESI-TOF) calcd. for $C_{16}H_{29}NO_4PS$ $[M + H]^+$ 362.1555; found 362.1528.

5.7.15 Dibutyl (*S*-ethylsulfonimidoyl)-4-methylbenzene phosphoroamidate (3fd):

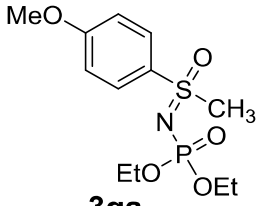


3fd

The reaction was carried out using general procedure. The title compound was obtained as transparent liquid, 172 mg, 92% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (80 % ethyl acetate) = 0.24.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, J = 8.3 Hz, 2H), 7.34 (d, J = 7.9 Hz, 2H), 4.02–3.92 (m, 4H), 3.40 (td, J = 13.4, 7.0 Hz, 2H), 2.43 (s, 3H), 1.63–1.60 (m, 2H), 1.53–1.52 (m, 2H), 1.37 (dd, J = 15.0, 7.5 Hz, 2H), 1.29 (dd, J = 15.1, 7.5 Hz, 2H), 1.20 (t, J = 7.4 Hz, 3H), 0.86 (dt, J = 20.2, 7.4 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 144.8, 134.9(d, J = 7.3 Hz), 129.9, 128.3, 66.3 (dd, $J_{C\text{-}P}$ = 6.4, 3.5 Hz), 53.0 (d, J = 4.8 Hz), 32.4 (dd, $J_{C\text{-}P}$ = 7.6, 5.0 Hz), 21.6, 18.8 (d, J = 7.9 Hz), 13.7 (d, J = 3.9 Hz), 7.9; **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.53. HRMS (ESI-TOF) calcd. for $C_{17}H_{30}NO_4PS$ $[M + H]^+$ 376.1711; found 376.1728.

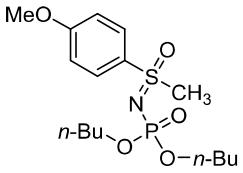
5.7.16 Diethyl (*S*-methylsulfonimidoyl)-4-methoxybenzene phosphoroamidate (3ga):



3ga

The reaction was carried out using general procedure. The title compound was obtained as transparent liquid, 142 mg, 89% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (80% ethyl acetate) = 0.24. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.89 (d, J = 8.9 Hz, 2H), 6.98 (d, J = 8.9 Hz, 2H), 4.07–3.00 (m, 4H), 3.83 (s, 3H), 3.28 (s, 3H), 1.25 (dt, J = 19.0, 7.1 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.8, 131.7, 129.5, 114.5, 62.6 (dd, $J_{C\text{-}P}$ = 6.0, 1.5 Hz), 55.7, 47.2 (d, J = 3.5 Hz), 16.1 (d, $J_{C\text{-}P}$ = 0.9 Hz); **^{31}P NMR (203 MHz, $CDCl_3$)** δ -1.91 (p, J =7.1 Hz). **HRMS** (ESI-TOF) calcd. for $C_{12}H_{20}NO_5PS$ $[M + H]^+$ 322.0878; found 322.0864.

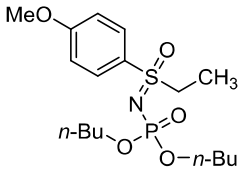
5.7.17 Dibutyl (*S*-methylsulfonimidoyl)-4-methoxybenzene phosphoroamidate (3gc):



3gc

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 172 mg, 91% yield. The product was isolated by silica-gel column chromatography using 50% ethyl acetate:hexane as an eluent. R_f (80% ethyl acetate) = 0.24. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.93 (d, J = 9.0 Hz, 2H), 7.02 (d, J = 9.0 Hz, 2H), 4.03–3.97 (m, 4H), 3.87 (s, 3H), 3.31 (s, 3H), 1.66–1.58 (m, 4H), 1.37 (ddd, J = 24.0, 15.1, 7.5 Hz, 4H), 0.90 (dt, J = 12.0, 7.4 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.9, 132.0 (d, J = 9.1 Hz), 129.6, 114.6, 66.5 (d, $J_{C\text{-}P}$ = 6.4 Hz), 55.8, 47.3 (d, J = 3.6 Hz), 32.4 (dd, $J_{C\text{-}P}$ = 7.6, 2.1 Hz),18.9 (d, J = 5.2 Hz), 13.8 (d, J = 1.9 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.71. **HRMS** (ESI-TOF) calcd. for $C_{16}H_{28}NO_5PS$ $[M + H]^+$ 378.1504 found 378.1512.

5.7.18 Dibutyl (*S*-ethylsulfonimidoyl)-4-methoxybenzene phosphoroamidate (3gd):

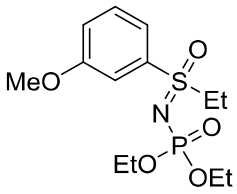


3gd

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 160 mg, 82% yield. The product was isolated by silica-gel column chromatography using 50% ethyl acetate:hexane as an eluent. R_f (80% ethyl acetate) = 0.24. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.87 (d, J = 9.0 Hz, 2H), 7.00 (d, J = 9.0 Hz, 2H), 3.99 (q, J = 6.6 Hz, 2H), 3.94 (q, J = 6.7 Hz, 2H), 3.86 (s, 3H), 3.39 (ddd, J = 14.4, 7.2, 2.6 Hz, 2H), 1.62 (dt, J = 14.5, 6.6 Hz, 2H), 1.54–1.53 (m, 2H), 1.38–1.36 (m, 2H), 1.31–1.29 (m, 2H), 1.21 (t, J = 7.3 Hz, 3H), 0.89 (t, J = 7.4 Hz, 3H), 0.85 (t, J = 7.4 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 163.8, 130.5, 129.2 (d, J = 7.4

Hz), 114.5, 66.3 (dd, $J_{C\text{-}P}$ = 6.3, 3.8 Hz), 55.8, 53.3 (d, J = 4.6 Hz), 32.4 (dd, $J_{C\text{-}P}$ = 7.5, 3.6 Hz), 18.8 (d, J = 7.3 Hz), 13.7 (d, J = 3.4 Hz), 8.0; **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.72 (p, J =7.5 Hz). **HRMS** (ESI-TOF) calcd. for $C_{17}H_{31}NO_5PS$ $[M + H]^+$ 392.1661; found 392.1636.

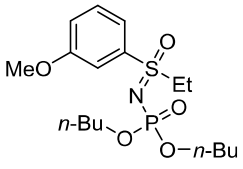
5.7.19 Diethyl (*S*-ethylsulfonimidoyl)-3-methoxybenzene phosphoroamidate (3ha):



3ha

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 139 mg, 83% yield. The product was isolated by silica-gel column chromatography using 50% ethyl acetate:hexane as an eluent. R_f (60% ethyl acetate) = 0.22. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.54–7.52 (m, 1H), 7.47–7.44 (m, 2H), 7.16–7.14 (m, 1H), 4.11–4.01 (m, 4H), 3.85 (s, 3H), 3.48–3.39 (m, 2H), 1.29 (t, J = 7.0 Hz, 3H), 1.23 (td, J = 7.2, 2.5 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 160.1, 139.1 (d, J = 7.2 Hz), 130.4, 120.4, 120.2, 112.8, 62.7 (dd, $J_{C\text{-}P}$ = 6.1, 3.1 Hz), 55.8, 52.9 (d, J = 4.5 Hz), 16.2 (dd, $J_{C\text{-}P}$ = 7.3, 5.8 Hz), 7.9; ^{31}P NMR (200 MHz, $CDCl_3$) δ -1.81. **HRMS** (ESI-TOF) calcd. for $C_{13}H_{23}NO_5PS$ $[M + H]^+$ 336.1035; found 336.1015.

5.7.20 Dibutyl (*S*-ethylsulfonimidoyl)-3-methoxybenzene phosphoroamidate (3hc):

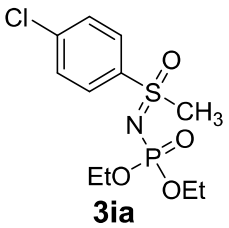


3hc

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 164 mg, 84% yield. The product was isolated by silica-gel column chromatography using 40% ethyl acetate:hexane as an eluent. R_f (60% ethyl acetate) = 0.24.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (ddd, J = 7.7, 1.6, 1.0 Hz, 1H), 7.48–7.44 (m, 2H), 7.16 (ddd, J = 8.2, 2.5, 0.9 Hz, 1H), 4.01 (q, J = 6.8 Hz, 2H), 3.95 (q, J = 6.7 Hz, 2H), 3.86 (s, 3H), 3.46–3.41 (m, 2H), 1.63 (dt, J = 14.8, 6.7 Hz, 2H), 1.56–1.53 (m, 2H), 1.40–1.36 (m, 2H), 1.32–1.28 (m, 2H), 1.24 (s, 3H), 0.90 (t, J = 7.4 Hz, 3H), 0.86 (t, J = 7.4 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 160.1, 139.2 (d, J = 7.0 Hz), 130.4, 120.4, 120.2, 112.8, 66.4 (dd, $J_{C\text{-}P}$ = 6.4, 3.9 Hz), 55.8, 53.0 (d, J = 4.8 Hz), 32.4 (dd, $J_{C\text{-}P}$ = 7.6, 5.3 Hz), 18.8 (d, J = 7.6 Hz), 13.7 (d, J = 5.0 Hz), 7.9; **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.68. **HRMS** (ESI-TOF) calcd. for $C_{17}H_{31}NO_5PS$ $[M + H]^+$ 392.1661; found 392.1636.

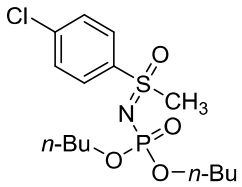
5.7.21 Diethyl (*S*-methylsulfonimidoyl)-4-chlorobenzene phosphoroamidate (3ia):



3ia

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 128 mg, 79% yield. The product was isolated by silica-gel column chromatography using 40% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.25. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.95 (d, J = 6.8 Hz, 2H), 7.55 (d, J = 6.8 Hz, 2H), 4.12–4.02 (m, 4H), 3.33 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H), 1.27 (t, J = 7.1 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 140.7, 139.0 (d, J = 8.8 Hz), 129.8, 128.9, 62.8 (dd, $J_{C\text{-}P}$ = 6.1, 3.5 Hz), 46.9 (d, J = 3.7 Hz), 16.2 (dd, $J_{C\text{-}P}$ = 7.5, 3.0 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -2.21. **HRMS** (ESI-TOF) calcd. for $C_{11}H_{18}ClNO_4PS$ $[M + H]^+$ 326.0377; found 326.0359.

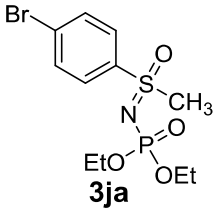
5.7.22 Dibutyl (*S*-methylsulfonimidoyl)-4-chlorobenzene phosphoroamidate (3ic):



3ic

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 152 mg, 80% yield. The product was isolated by silica-gel column chromatography using 40% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.26. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.96–7.95 (m, 2H), 7.55–7.54 (m, 2H), 4.00 (dq, J = 22.1, 6.7 Hz, 4H), 3.32 (s, 3H), 1.66–1.57 (m, 4H), 1.41–1.31 (m, 4H), 0.89 (dt, J = 12.1, 7.4 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 140.7, 139.1 (d, J = 8.5 Hz), 129.8, 129.0, 66.6 (dd, $J_{C\text{-}P}$ = 6.4, 2.6 Hz), 46.9 (d, J = 3.9 Hz), 32.4 (dd, $J_{C\text{-}P}$ = 7.5, 2.7 Hz), 18.8 (d, J = 5.0 Hz), 13.7 (d, J = 2.7 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -2.05. HRMS (ESI-TOF) calcd. for $C_{15}H_{26}ClNO_4PS$ $[M + H]^+$ 382.1009; found 382.0987.

5.7.23 Diethyl (*S*-methylsulfonimidoyl)-4-bromobenzene phosphoroamidate (3ja):

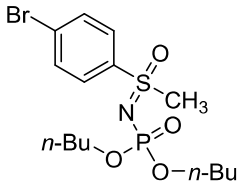


3ja

The reaction was carried out using general procedure. The title compound was obtained as brown liquid, 138 mg, 75% yield. The product was isolated by silica-gel column chromatography using 50% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.20. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.89 (d, J = 8.8 Hz, 2H), 7.72 (d, J = 8.8 Hz, 2H), 4.15–4.02 (m, 4H), 3.34 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H), 1.28 (t, J = 7.1 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 139.5 (d, J = 8.6 Hz), 132.8, 129.3, 129.0, 62.9 (dd, $J_{C\text{-}P}$ = 6.0, 3.5 Hz), 46.9 (d, J = 3.7 Hz), 16.2 (dd, $J_{C\text{-}P}$ = 7.5, 3.3 Hz); **^{31}P NMR**

(200 MHz, $CDCl_3$) δ -2.22. **HRMS** (ESI-TOF) calcd. for $C_{11}H_{18}BrNO_4PS$ $[M + H]^+$ 369.9878; found 369.9856.

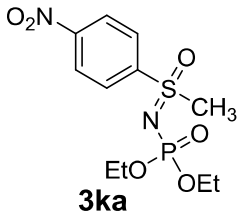
5.7.24 Dibutyl (*S*-methylsulfonimidoyl)-4-bromobenzene phosphoroamidate (3jc):



3jc

The reaction was carried out using general procedure. The title compound was obtained as brown liquid, 212 mg, 78% yield. The product was isolated by silica-gel column chromatography using 50% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.22. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.85–7.83 (m, 2H), 7.68–7.67 (m, 2H), 3.95 (dq, J = 20.3, 6.7 Hz, 4H), 3.29 (s, 3H), 1.61–1.53 (m, 4H), 1.34–1.28 (m, 4H), 0.85 (dt, J = 11.1, 7.4 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 139.5 (d, J = 8.4 Hz), 132.7, 128.9, 66.5 (dd, $J_{C\text{-}P}$ = 6.4, 2.0 Hz), 46.8 (d, J = 3.9 Hz), 32.2 (dd, $J_{C\text{-}P}$ = 7.5, 2.4 Hz), 18.7 (d, J = 4.5 Hz), 13.6 (d, J = 1.9 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -2.10 (p, J =6.7 Hz). **HRMS** (ESI-TOF) calcd. for $C_{15}H_{26}BrNO_4PS$ $[M + H]^+$ 426.0504; found 426.0496.

5.7.25 Diethyl (*S*-methylsulfonimidoyl)-4-nitrobenzene phosphoroamidate (3ka):

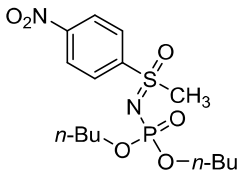


3ka

The reaction was carried out using general procedure. The title compound was obtained as pale yellow liquid, 119 mg, 71% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.22. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.42 (d, J = 8.8 Hz, 2H), 8.24 (d, J = 8.8 Hz, 2H), 4.14–4.04 (m, 4H), 3.39 (s, 3H), 1.33 (t, J = 7.0 Hz, 3H), 1.28 (t, J = 5.9 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ

151.0, 146.2 (d, J = 8.0 Hz), 129.1, 124.7, 63.1 (t, $J_{C\text{-}P}$ = 6.0 Hz), 46.6 (d, J = 4.1 Hz), 16.2 (dd, $J_{C\text{-}P}$ = 7.4, 2.8 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -2.67 (p, J =7.6 Hz). **HRMS** (ESI-TOF) calcd. for $C_{11}H_{18}N_2O_6PS$ $[M + H]^+$ 337.0623; found 337.0599.

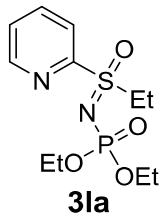
5.7.26 Dibutyl (*S*-methylsulfonimidoyl)-4-nitrobenzene phosphoroamidate (3kc):



3kc

The reaction was carried out using general procedure. The title compound was obtained as yellow oil, 148 mg, 76% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.24. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.42–8.40 (m, 2H), 8.24–8.22 (m, 2H), 4.00 (dq, J = 20.3, 6.7 Hz, 4H), 3.38 (s, 3H), 1.66–1.57 (m, 4H), 1.36 (ddd, J = 25.2, 15.0, 7.5 Hz, 4H), 0.92–0.86 (m, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 150.9, 146.2 (d, J = 7.8 Hz), 129.0, 124.7, 66.7 (dd, $J_{C\text{-}P}$ = 6.1, 5.4 Hz), 46.6 (d, J = 4.2 Hz), 32.3 (dd, $J_{C\text{-}P}$ = 7.5, 2.5 Hz), 18.8 (d, J = 4.6 Hz), 13.7 (d, J = 2.9 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -2.50. **HRMS** (ESI-TOF) calcd. for $C_{15}H_{26}N_2O_6PS$ $[M + H]^+$ 393.1249; found 393.1240.

5.7.27 3.27 Diethyl (*S*-methylsulfonimidoyl)pyridine phosphoroamidate (3la):

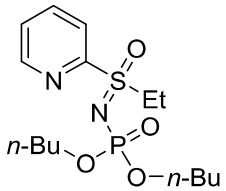


3la

The reaction was carried out using general procedure. The title compound was obtained as pale yellow oil, 130 mg, 85% yield. The product was isolated by silica-gel column chromatography using 70% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate, 3 times) = 0.22. **^{1}H NMR (500 MHz, CDCl3)** δ 8.73 (d, J = 4.3 Hz,

1H), 8.23 (d, J = 7.9 Hz, 1H), 7.97 (t, J = 7.7 Hz, 1H), 7.56–7.54 (m, 1H), 4.04 (dd, J = 14.1, 7.0 Hz, 4H), 3.72 (qd, J = 14.3, 7.1 Hz, 2H), 1.29–1.24 (m, 9H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 156.4 (d, J = 7.1 Hz), 150.1, 138.3, 127.4, 123.2, 62.7 (t, $J_{C\text{-}P}$ = 5.8 Hz), 48.5 (d, J = 5.8 Hz), 16.2 (d, $J_{C\text{-}P}$ = 7.5 Hz), 7.3; **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.81. **HRMS** (ESI-TOF) calcd. for $C_{11}H_{20}N_2O_4PS$ $[M + H]^+$ 307.0881; found 307.0862.

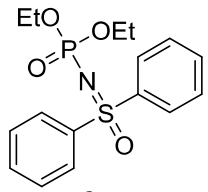
5.7.28 3.28 Dibutyl (*S*-methylsulfonimidoyl) pyridine phosphoroamidate (3lc):



3lc

The reaction was carried out using general procedure. The title compound was obtained as yellow oil, 163 mg, 90% yield. The product was isolated by silica-gel column chromatography using 80% ethyl acetate:hexane as an eluent. R_f (100% ethyl aceatae) = 0.24. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.70 (d, J = 4.3 Hz, 1H), 8.21 (d, J = 7.9 Hz, 1H), 7.95 (t, J = 7.8 Hz, 1H), 7.53 (dd, J = 7.4, 4.8 Hz, 1H), 4.98–3.93 (m, 4H), 3.69 (dt, J = 14.9, 7.3 Hz, 2H), 1.58 (dd, J = 14.5, 7.1 Hz, 4H), 1.34 (dt, J = 12.1, 7.3 Hz, 4H), 1.24 (t, J = 7.4 Hz, 3H), 0.87 (td, J = 7.4, 3.4 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 156.5 (d, J = 7.1 Hz), 150.0, 138.2, 127.3, 123.1, 66.3 (dd, $J_{C\text{-}P}$ = 6.2, 4.2 Hz), 48.4 (d, J = 5.7 Hz), 32.3 (d, $J_{C\text{-}P}$ = 7.5 Hz), 18.8, 13.7, 7.2; **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.67 (p, J =6.9 Hz). **HRMS** (ESI-TOF) calcd. for $C_{15}H_{28}N_2O_4PS$ $[M + H]^+$ 363.1507; found 363.1487.

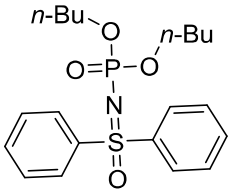
5.7.29 Diethyl (*S*-diphenylsulfonimidoyl) phosphoroamidate (3ma):



3ma

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 148 mg, 84% yield. The product was isolated by silica-gel column chromatography using 70% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.24. **^{1}H NMR (500 MHz, CDCl3)** δ 8.02–8.00 (m, 4H), 7.57–7.53 (m, 2H), 7.51–7.48 (m, 4H), 4.07–3.98 (m, 4H), 1.19 (td, J = 7.1, 0.7 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 141.8 (d, J = 6.6 Hz), 133.3, 129.3, 127.7, 62.7 (d, $J_{C\text{-}P}$ = 6.2 Hz), 16.1 (d, $J_{C\text{-}P}$ = 7.5 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -2.35. **HRMS** (ESI-TOF) calcd. for $C_{16}H_{21}NO_4PS$ $[M + H]^+$ 354.0929; found 354.0911.

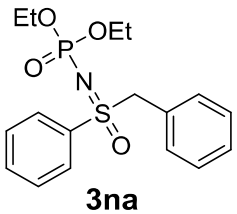
5.7.30 Dibutyl (*S*-diphenylsulfonimidoyl) phosphoroamidate (3mc):



3mc

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 174 mg, 85% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.25. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 8.01 (d, J = 8.0 Hz, 4H), 7.54 (t, J = 6.8 Hz, 2H), 7.49 (t, J = 7.6 Hz, 4H), 3.99–3.92 (m, 4H), 1.54–1.48 (m, 4H), 1.27 (dd, J = 15.0, 7.5 Hz, 4H), 0.84 (t, J = 7.4 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 141.9 (d, J = 6.7 Hz), 133.2, 129.3, 127.7, 66.4 (d, $J_{C\text{-}P}$ = 6.5 Hz), 32.3 (d, $J_{C\text{-}P}$ = 7.5 Hz), 18.8, 13.7; **^{31}P NMR (200 MHz, $CDCl_3$)** δ -2.19. **HRMS** (ESI-TOF) calcd. for $C_{20}H_{29}NO_4PS$ $[M + H]^+$ 410.1555; found 410.1541.

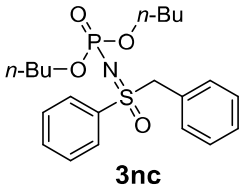
5.7.31 Diethyl (*S*-benzylsulfonimidoyl)benzene phosphoroamidate (3na):



3na

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 167 mg, 91% yield. The product was isolated by silica-gel column chromatography using 50% ethyl acetate:hexane as an eluent. R_f (80% ethyl acetate) = 0.24. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.62 (dd, J = 8.5, 1.2 Hz, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.42–7.39 (m, 2H), 7.25 (d, J = 8.5 Hz, 1H), 7.17 (t, J = 7.6 Hz, 2H), 6.99 (d, J = 7.1 Hz, 2H), 4.71 (d, J = 13.8 Hz, 1H), 4.65 (d, J = 13.8 Hz, 1H), 4.13–4.01 (m, 4H), 1.30 (t, J = 7.1 Hz, 3H), 1.23 (d, J = 7.1 Hz, 3H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 136.9 (d, J = 8.9 Hz), 133.8, 131.3, 128.9 (d, J = 10.1 Hz), 128.7 (s), 128.4 (s), 127.9 (s), 64.7 (d, J = 3.2 Hz), 62.8 (dd, $J_{C\text{-}P}$ = 6.1, 3.0 Hz), 16.1 (dd, $J_{C\text{-}P}$ = 7.5, 3.4 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.62. **HRMS** (ESI-TOF) calcd. for $C_{17}H_{23}NO_4PS$ $[M + H]^+$ 368.1085; found 368.1069.

5.7.32 Dibutyl (*S*-benzylsulfonimidoyl)benzene phosphoroamidate (3nc):

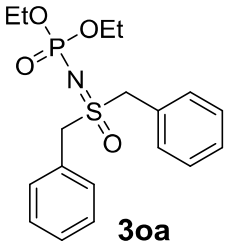


3nc

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 171 mg, 81% yield. The product was isolated by silica-gel column chromatography using 50% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.25. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.61 (dd, J = 8.4, 1.1 Hz, 2H), 7.57–7.54 (m, 1H), 7.39 (dd, J = 11.7, 4.0 Hz, 2H), 7.24 (dd, J = 10.7, 4.1 Hz, 1H), 7.15 (t, J = 7.6 Hz, 2H), 6.98 (d, J = 7.7 Hz, 2H), 4.70–4.54 (m, 2H), 4.02–3.93 (m, 4H), 1.62–1.53 (m, 4H), 1.33 (ddd,

J = 29.5, 15.0, 7.5 Hz, 4H), 0.86 (dt, J = 15.0, 7.4 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 136.9 (d, J = 8.5 Hz), 133.7, 131.2, 128.8 (d, J = 9.0 Hz), 128.6, 128.3, 127.9, 66.5 (dd, $J_{C\text{-}P}$ = 6.3, 4.7 Hz), 64.7 (d, J = 3.4 Hz), 32.2 (dd, $J_{C\text{-}P}$ = 7.6, 3.5 Hz), 18.7 (d, J = 6.4 Hz), 13.6 (d, J = 4.2 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.51. **HRMS** (ESI-TOF) calcd. for $C_{21}H_{31}NO_4PS$ $[M + H]^+$ 424.1711; found 424.1694.

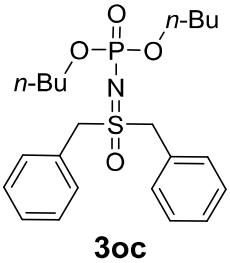
5.7.33 Diethyl (*S*-dibenzylsulfonimidoyl) phosphoroamidate (3oa):



3oa

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 171 mg, 90% yield. The product was isolated by silica-gel column chromatography using 50% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.25. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.43–7.40 (m, 4H), 7.38 (td, J = 4.4, 1.5 Hz, 6H), 4.47 (d, J = 13.7 Hz, 2H), 4.38 (dd, J = 13.7, 1.5 Hz, 2H), 3.95–3.89 (m, 4H), 1.21 (td, J = 7.1, 0.7 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 131.5, 129.3, 128.9, 127.1, 62.6 (d, $J_{C\text{-}P}$ = 6.2 Hz), 59.5 (d, J = 3.8 Hz), 16.1 (d, $J_{C\text{-}P}$ = 7.5 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -2.55. **HRMS** (ESI-TOF) calcd. for $C_{18}H_{25}NO_4PS$ $[M + H]^+$ 382.1242; found 382.1231.

5.7.34 Dibutyl (*S*-dibenzylsulfonimidoyl) phosphoroamidate (3oc):

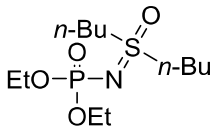


3oc

The reaction was carried out using general procedure. The title compound was obtained as pale yellow oil, 190 mg, 87% yield. The product was isolated by silica-gel column chromatography using 40% ethyl acetate:hexane as an eluent. R_f (70% ethyl acetate) = 0.27.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (dd, J = 7.0, 2.6 Hz, 4H), 7.39–7.37 (m, 6H), 4.47 (d, J = 13.7 Hz, 2H), 4.38 (dd, J = 13.7, 1.4 Hz, 2H), 3.85 (qd, J = 6.7, 1.4 Hz, 4H), 1.58–1.53 (m, 4H), 1.35–1.30 (m, 4H), 0.87 (t, J = 7.4 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 131.5, 129.3, 128.8, 127.2, 66.4 (d, $J_{C\text{-}P}$ = 6.5 Hz), 59.5 (d, J = 3.8 Hz), 32.3 (d, $J_{C\text{-}P}$ = 7.6 Hz), 18.8, 13.7; **^{31}P NMR (200 MHz, $CDCl_3$)** δ -2.27. **HRMS** (ESI-TOF) calcd. for $C_{22}H_{33}NO_4PS$ $[M + H]^+$ 438.1868; found 438.1859.

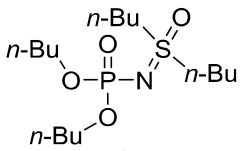
5.7.35 Diethyl (*S*-dibutylsulfonimidoyl) phosphoroamidate (3pa):



3pa

The reaction was carried out using general procedure. The title compound was obtained as pale yellow liquid, 122 mg, 78% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (80% ethyl acetate) = 0.22. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 4.02 (p, J = 7.1 Hz, 4H), 3.25–3.17 (m, 4H), 1.82–1.76 (m, 4H), 1.43 (dt, J = 14.7, 7.4 Hz, 4H), 1.27 (t, J = 7.1 Hz, 6H), 0.92 (t, J = 7.4 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 62.5 (d, $J_{C\text{-}P}$ = 6.0 Hz), 53.8 (d, J = 4.5 Hz), 24.3, 21.6, 16.2 (d, $J_{C\text{-}P}$ = 7.5 Hz), 13.6; **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.90. **HRMS** (ESI-TOF) calcd. for $C_{12}H_{29}NO_4PS$ $[M + H]^+$ 314.1555; found 314.1537.

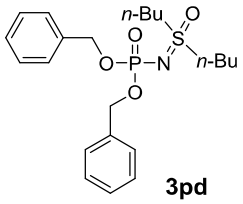
5.7.36 Dibutyl (*S*-dibutylsulfonimidoyl) phosphoroamidate (3pc):



3pc

The reaction was carried out using general procedure. The title compound was obtained as transparent oil, 150 mg, 81% yield. The product was isolated by silica-gel column chromatography using 60% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.24. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 3.92 (dd, J = 9.0, 3.7 Hz, 4H), 3.22–3.13 (m, 4H), 1.76–1.71 (m, 4H), 1.58 (d, J = 6.3 Hz, 4H), 1.41–1.33 (m, 8H), 0.89 (dddd, J = 14.5, 8.0, 7.3, 3.9 Hz, 12H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 66.2 (d, $J_{C\text{-}P}$ = 5.8 Hz), 53.7, 32.3 (d, $J_{C\text{-}P}$ = 7.2 Hz), 24.3, 21.5, 18.8, 13.6 (d, J = 9.8 Hz); **^{31}P NMR (200 MHz, $CDCl_3$)** δ -1.88. **HRMS** (ESI-TOF) calcd. for $C_{16}H_{37}NO_4PS$ $[M + H]^+$ 370.2181; found 370.2165.

5.7.37 Dibenzyl (*S*-dibutylsulfonimidoyl) phosphoroamidate (3pd):



3pd

The reaction was carried out using general procedure. The title compound was obtained as white solid, 166 mg, 76% yield. The product was isolated by silica-gel column chromatography using 50% ethyl acetate:hexane as an eluent. R_f (100% ethyl acetate) = 0.22. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.36–7.27 (m, 10H), 5.01 (p, J = 11.8 Hz, 4H), 3.24–3.09 (m, 4H), 1.76 (dd, J = 15.3, 7.6 Hz, 4H), 1.39 (dd, J = 14.5, 7.2 Hz, 4H), 0.90 (t, J = 7.2 Hz, 6H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 136.8 (d, J = 7.7 Hz), 128.3, 128.0, 127.8, 68.1 (d, J = 5.8 Hz), 54.0–53.7 (m), 29.7, 24.3, 21.6, 13.6. **^{31}P NMR (200 MHz, $CDCl_3$)** δ 0.73. **HRMS** (ESI-TOF) calcd. for $C_{22}H_{33}NO_4$ $[M + H]^+$ 438.1868; found 438.1854.

5.8 Spectral Data of Product:

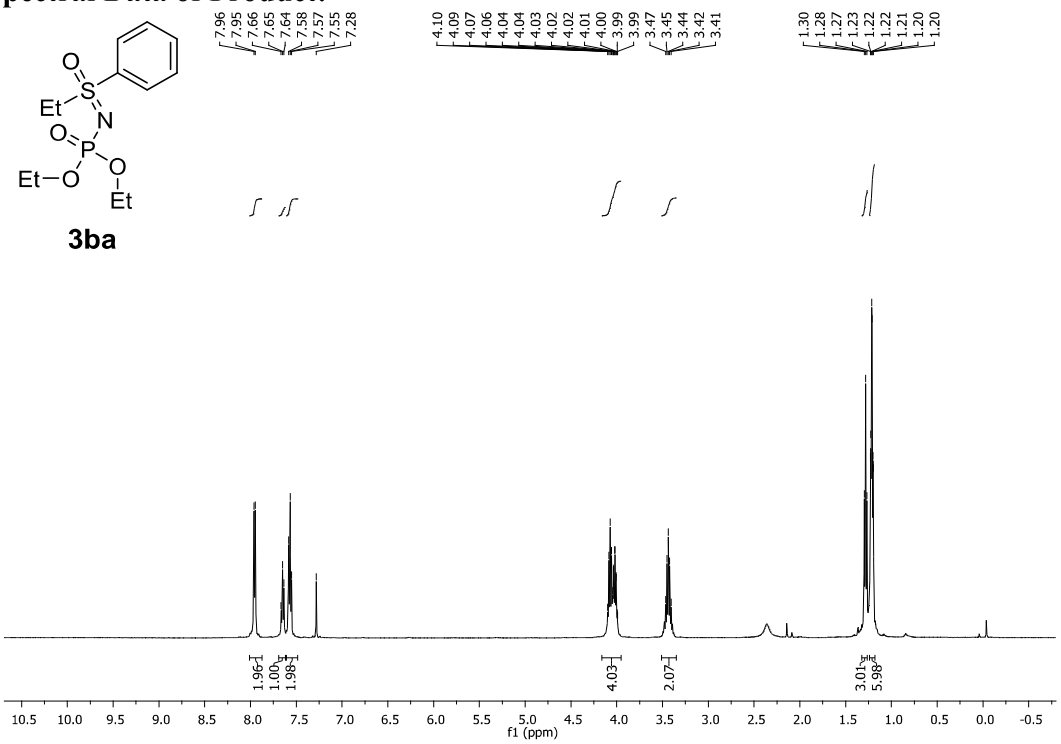


Figure 5.2 ^{1}H NMR for **3ba**

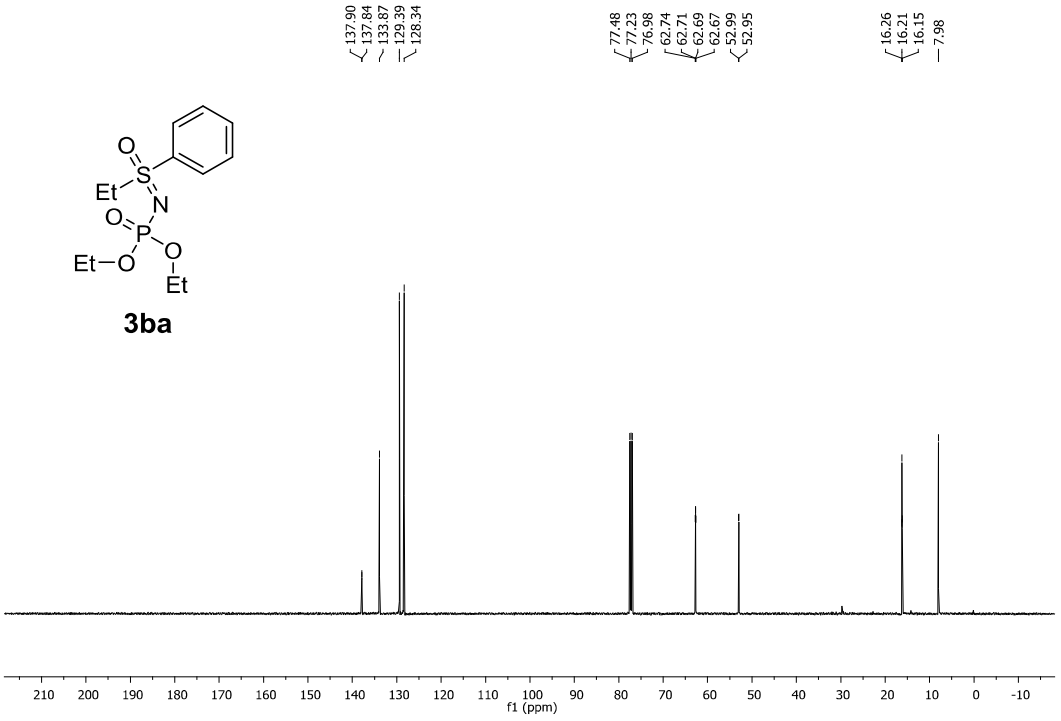


Figure 5.3 ^{13}C NMR for **3ba**

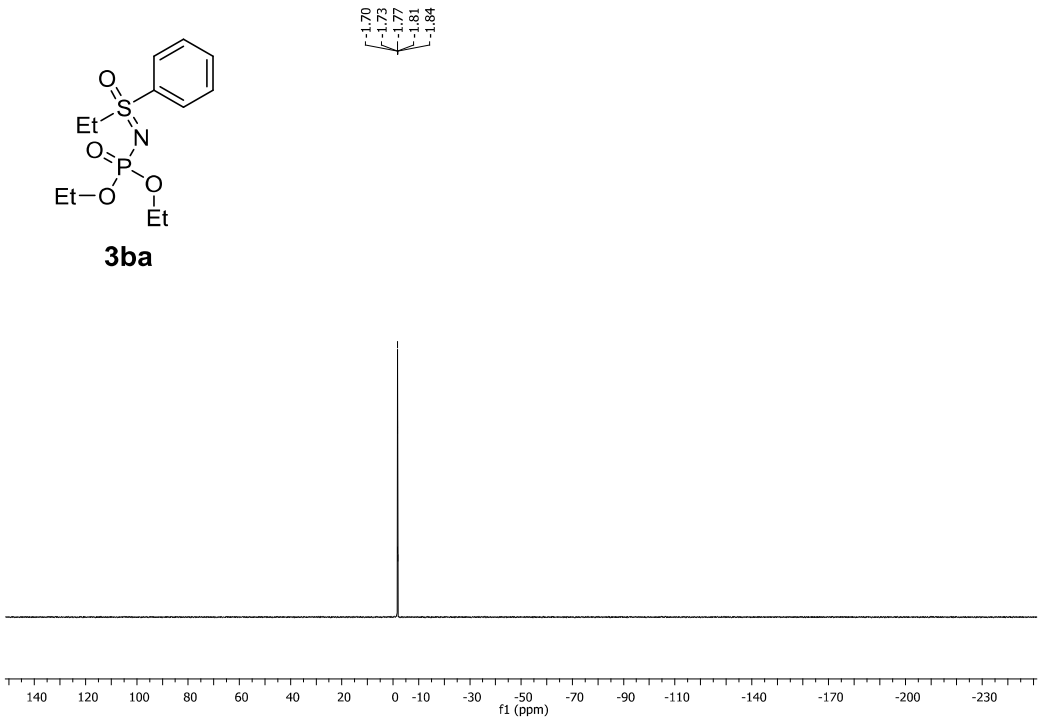


Figure 5.4 ^{31}P NMR for **3ba**

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