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Copper(I)-Induced Sulfenylation of H-Phosphonates, H-Phosphonites and Phosphine Oxides with Aryl/alkylsulfonylhydrazides as a Thiol Surrogate

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Abstract: Aerobic dehydrogenative sulfenylation of H-phosphonites, and phosphine oxides with aryl/alkylsulfonyl hydrazides catalyzed by a sub-stoichiometric amount of copper iodide has been accomplished. This protocol is compatible with functional groups, and results in various thiophosphate derivatives in good to high yields.

Keywords: copper iodide; sulfenylation; sulfonylhydrazides; thiol surrogate; thiophosphates

Introduction

Copper-catalyzed carbon-carbon bond, carbon-heteroatom bond, and heteroatom-heteroatom bond forming reactions have emerged as a method of choice and this can be ascribed to the functional group compatibility of copper metal as well as its easy accessibility, and cost-effectiveness.[1] Recently, single electron transfer initiated, Cu-catalyzed dehydrogenative cross-coupling transformations have been developed to access various functional molecules.[2]

Furthermore, dioxygen acts as an oxidant in Cu-catalyzed dehydrogenative reactions, thereby generating a truly environmentally benign water molecule as by-product. This strategy offers an appealing alternative to cross-coupling reactions whereby activation of the corresponding cross-coupling reaction partners by pre-functionalization is circumvented. The copper-catalyzed carbon-carbon bond[3] and carbon-heteroatom bond[4] forming reactions are fairly well established but their respective heteroatom-heteroatom bond[5] forming reactions are rather scarce. In particular, P–S bond formation reactions are limited owing to their exceptional oxidative reactivity, consequently leading to dimerization. The derivatives of thiophosphates display diverse biological activities, for example, as pesticides, insecticides, enzyme modifiers, and potential HIV-1 and ACHE inhibitors.[6]

The prominent routes for the synthesis of thiophosphorus compounds include (i) Michaelis–Arbuzov reaction of trisubstituted derivatives of phosphites with alkyl- or arylsulfonyl chlorides;[7] (ii) reaction of H-phosphonates with various sulfenyl chlorides,[8] sulfenyl cyanides,[9] and substituted disulfides;[10] and (iii) condensation of phosphorochloridates with thiols or their metal salts (Figure 1).[11] Recently, an interesting Cu-catalyzed aerobic dehydrogenative coupling of H-phosphonates with various substituted aryl thiols under basic media leading to thiophosphates has been reported (Figure 1).[12] However, methods for the synthesis of the thiophosphate class of compounds are extremely limited due to oxidative self-dimerizations catalyzed by air/metal complexes in the presence of a base. Additionally, the high propensity of metal coordination by sulfur hampers the use of metal catalysis, thereby restricting the scope of application. Hence, there is still great need for the development of a functional group compatible and convenient protocol to produce various thiophosphate derivatives.

Results and Discussion

Consistent with our continued interest in developing base-free Cu-catalyzed P–C bond formation routes,[13] we report our findings regarding dehydrogenative cross-coupling of H-phosphonates with sulfonylhydrazides as aryl/alkyl thio surrogates. Initially, 1 equiv. of diethyl H-phosphonate **1a**, and 1.2 equiv. of tosylhydrazide **2a** were allowed to react in the presence of

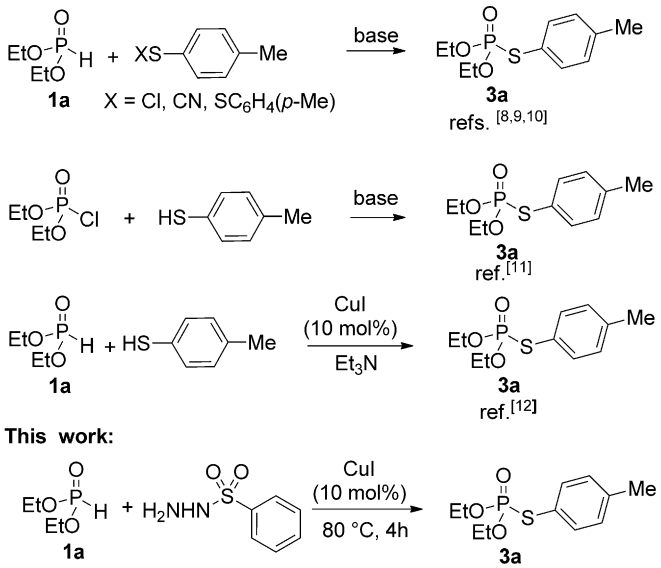


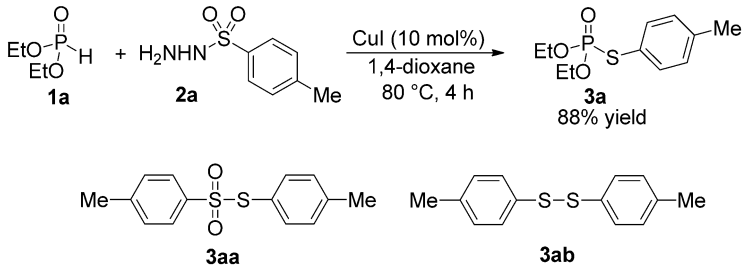
Figure 1. Prior art in P–S bond formation.

molecular iodine (10 mol%) in refluxing ethanol under an atmosphere of air in analogy to the literature report.[2b] No trace of the anticipated sulfenylated product **3a** was observed; instead dimerized compounds **3aa** and **3ab** were isolated (entry 1, Table 1).

Replacing ethanol by 1,4-dioxane, under otherwise identical conditions, resulted in an identical set of compounds with varying yields (entry 2, Table 1).[14] Performing the reaction with a catalytic amount of $PdCl_2$ in place of I_2 under the same conditions also did no yield of the required compound **3a** (entry 3, Table 1).

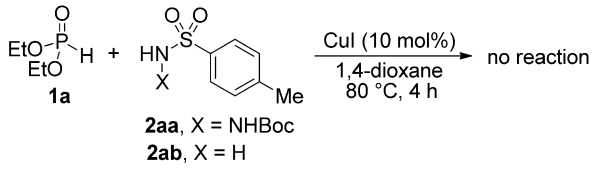
After considerable experimentation, use of 1 equiv. of diethyl H-phosphonate **1a**, and 1.2 equiv. of tosylhydrazine **2a** in the presence of 10 mol% of CuI in dioxane under heating at 80 °C provided the desired sulfenylated product **3a** in 88% isolated yield (entry 11, Table 1). In this process, various copper salts have been examined. Although all copper salts initiated the reaction (entries 4–11, Table 1), CuI was found to

Table 1. Screening of various catalysts and conditions for dehydrogenate cross-coupling of diethyl H-phosphonate with tosylhydrazide.[a]



Entry	Catalyst (10 mol%)	Solvent	**3a** (yield [%])[b]
1	I_2	EtOH	**3aa** (20), **3ab** (30)
2	I_2	dioxane	**3aa** (10), **3ab** (20)
3	$PdCl_2$	dioxane	NR[c]
4	$Cu(OAc)_2$	dioxane	64
5	$CuCl_2$	dioxane	58
6	CuCN	dioxane	80
7	$Cu(CH_3CN)_4PF_6$	dioxane	76
8	CuCl	dioxane	72
9	CuBr	dioxane	83
10	CuI	dioxane	50[d]
11	**CuI**	**dioxane**	**88**[e]
12	CuI(5)	dioxane	50[f]
13	CuI	CH_3CN	60
14	CuI	DMF	40
15	CuI	toluene	45
16	CuI	DCE	52
17	CuI	neat	80

[a] All reactions were carried out using 1 mmol scale using **1a** (1 mmol), **2a** (1.2 mmol), CuI (0.1 mmol) in 2 mL of dioxane heating at 80 °C for 4 h in the open air.
[b] Isolated yield, but not optimized.
[c] NR = No reaction.
[d] Reaction carried out at 50 °C.
[e] This reaction also carried out 20 mmol scale with heating at 80 °C for 12 h in the open air.
[f] Reaction carried out with 5 mol% catalyst at 80 °C.



Scheme 1. Cu(I)-promoted dehydrogenative cross-coupling of *N*-substituted sulfonyl hydrazines.

be the most effective catalyst regarding the observed product **3a** formation (88% yield). Meanwhile, 5 mol% catalyst loading led to a reduced yield (entry 12, Table 1). Solvent screening revealed that dioxane is optimal (entries 13–16, Table 1). Remarkably, the reaction proceeded under solvent-free conditions, resulting in **3a**, albeit in lower yield (entry 17, Table 1). The reaction proved to be fairly sensitive to temperature, yielding 50% when the temperature was reduced from 80 to 60 °C, whereas with higher temperature (>80 °C) product decomposition was observed. Using deaerated dioxane under an argon atmosphere furnished the product **3a** in low yield (15%), indicating participation of dioxygen in the reaction. In a blank reaction in the absence of CuI, no trace of product **3a** was observed.

In order to appraise the necessity of the $-NHNH_2$ functionality, a Boc-protected sulfonylhydrazide, **2aa**, was prepared and subjected to the standard reaction conditions in the presence of **1a**. No trace of the required compound **3a** was observed. Only starting materials were recovered. Similarly, the reaction of benzenesulfonamide **2ab** with **1a** also resulted in no reaction, indicating that the $-NHNH_2$ group is indispensable for the reaction to proceed (Scheme 1).

With the optimum conditions in hand, the scope of this new reaction was investigated and the corresponding results are summarized in Table 2. Looking at the tabulated results, the sulfenylation substrate scope is well established. The reaction is not only compatible with various substitutions on phosphorus, but also maintains the substitution pattern of the sulfonylhydrazine aromatic nucleus. Moreover, the sulfonylhydrazide aromatic nucleus functional group substitution proved to be inconsequential to the reaction outcome, as both **2f** and **2k**, bearing electron-donating methyl and electron-withdrawing fluoride groups, respectively, resulted in good yields (**3f** and **3k**, Table 2).

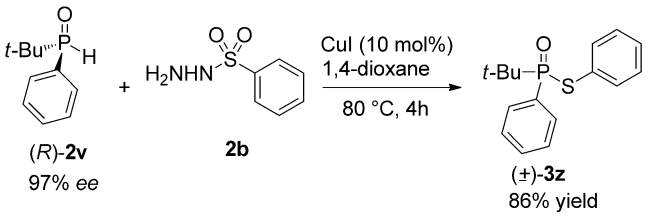
Significantly, a highly polar carboxylic acid substituted arylsulfonylhydrazide performed well under the standard protocol, affording carboxylic acid possessing thiophosphate **3m** in 75% yield (Table 2). Also, 1,3-disulfonylhydrazide **2n** underwent the sulfenylation reaction with moderate yield (**3n**, Table 2). It is noteworthy that methyl as well as butyl thiophosphates, **3o** and **3p** (Table 2), were efficiently generated employing the respective alkylsulfonylhydrazides.

These examples reveal the potential utility of this methodology for the preparation of various alkyl thiophosphates that are used as pesticides.[6e] Also, benzylhydrazide **2q** underwent the sulfenylation reaction with good yield (**3q**, Table 2).

This methodology was extended to coupling of various aryl-/alkylphosphine oxides. Bis(*meta*-methoxy)-phenylphosphine oxide **2t** and even dibutylphosphine oxide **2u** participated in the sulfenylation reaction under otherwise identical conditions as above and delivered the corresponding thiophosphates **3t** and **3u** in excellent yields (Table 2). Ethyl phenylphosphinate **2w** underwent coupling yielding the thiophosphate **3w** in 85%. Menthyl phenylphosphinate **2x**[15] also served as good substrate to produce the corresponding thiophosphate **3x** as a diastereomeric mixture (65:35) in high yield (Table 2). Interestingly, diphenylphosphine-borane, **2y** proceeded well for sulfenylation, giving rise to thiophosphine-borane **3y** in 85% yield (Table 2).

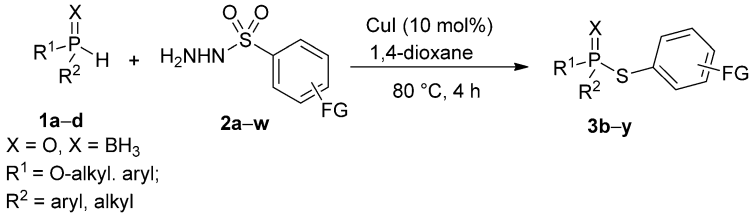
Nucleophilic substitution reactions of chiral tetracoordinate secondary phosphorus compounds having a P–H bond can possibly result in racemiz6ation.[13a,16] In the light of these observations, we explored whether the copper-catalyzed dehydrogenative cross-coupling reaction proceeds with retention or inversion of the configuration at phosphorus. Consequently, enantioenriched (*R*)-**2v** was reacted with **2b** under the typical reaction conditions. The desired product (±)-**3z** was obtained in 86% yield with racemization indicating that the configuration of phosphorus is not preserved during the transformation (Scheme 2).

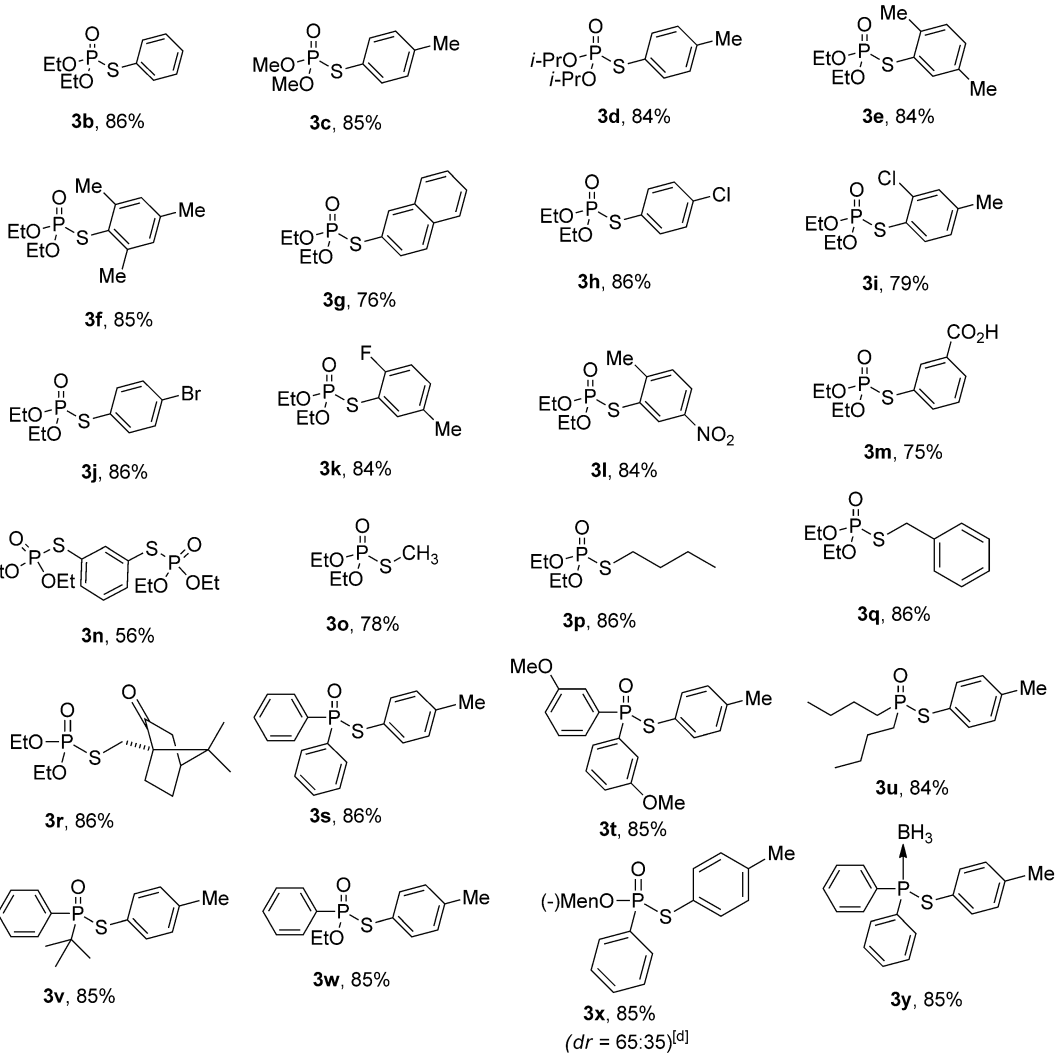
A plausible mechanism is proposed by analogy with dehydrogenative cross-coupling reactions.[2b,c] Initially, the oxidation of Cu(I) by molecular oxygen generates the copper(II) peroxo species, [**A**] which then dissociates in the presence of sulfonylhydrazide resulting in metallo-organic peroxide [**B**] and HO-Cu(II). Then, sequential removal of hydrogen and oxygen atoms from the putative intermediate [**B**] could lead to thiodiazonium [**C**]. The nucleophilic substitution reaction of phosphite anion, [**D**], on thiodiazonium [**C**] eventually results in the desired thiophosphate, **3a** (Scheme 3).



Scheme 2. Sulfenylation of a chiral phosphine oxide.

Table 2. Synthesis of thiophosphonatederivatives.[a,b,c]

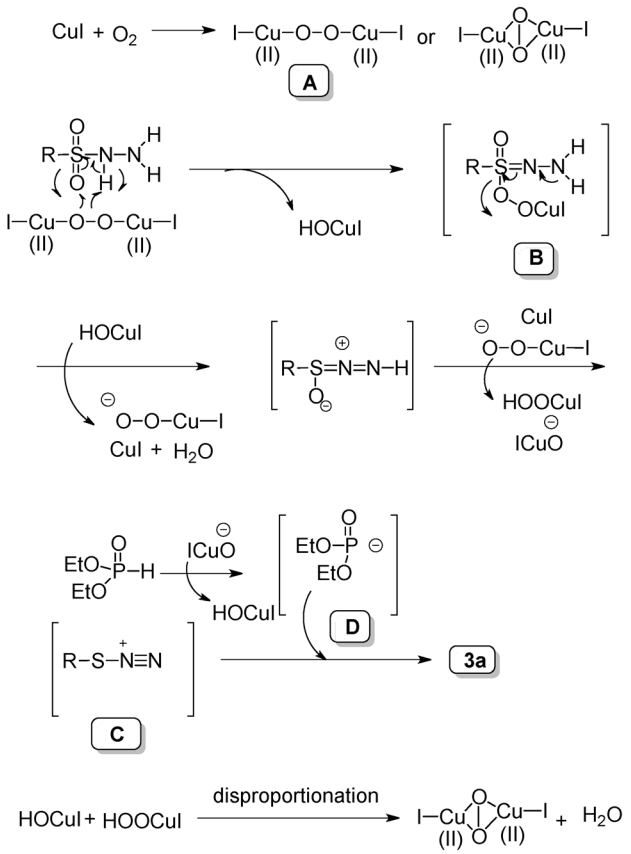




[a] All reactions were carried out using 1 equiv. of phosphorus compound, 1.2 equiv. of aryl/alkylsulfonylhydrazide and 0.1 equiv. of CuI in dioxane heating at 80 °C for 4 h in the open air.
[b] Isolated yields.
[c] All compounds were fully characterized.
[d] Diastereomeric ratio was determined by ^{31}P NMR and also analyzed on a chiral AS column by HPLC.

Conclusions

In conclusion, we have successfully developed a mild and base-free sulfenylation of aryl/alkyl H-phosphonates and phosphine oxides using odourless, air-stable sulfonylhydrazides as a thiol surrogate. A series of sterically and electronically divergent phosphorus derivatives and aryl/alkylsulfonylhydrazides participated in the coupling reaction and the corresponding products were obtained in high yields. The striking feature



Scheme 3. Proposed Cu(I)-promoted dehydrogenative cross-coupling cycle.

of this reaction is that alkyl thiophosphates are readily accessible through this protocol. To the best of our knowledge this is the first report on sulfenylation of phosphorus through aryl/alkylsulfonylhydrazides. Further work is in progress to broaden the scope of this reaction.

Experimental Section

General Methods

All reactions were conducted under an open air atmosphere. Apparatus used for reactions are oven-dried. 1,4-Dioxane and other solvents were used as received. ^{1}H NMR spectra were recorded at 300, 400 and 500 MHz and ^{13}C NMR 75 and 125 MHz in $CDCl_3$. ^{31}P spectra were recorded at 200 MHz in $CDCl_3$. *J* values were recorded in hertz and abbreviations used were *s* = singlet, *d* = doublet, *m* = multiplet, br = broad, *dd* = doublet of doublet. Chemical shifts (δ) are reported relative to TMS ($\delta = 0.0$) as an internal standard. IR (FT-IR) spectra were measured as KBr pellets or as films. Mass spectral data were compiled using MS (ESI), HR-MS mass spectrometers. Optical rotations were recorded on a high sensitive polarimeter with 10 mm cell. Column chromatography was carried out using Silica gel 100–200 mesh (commercial suppliers).

Typical Procedure for Synthesis of *O,O*-Diethyl *S*-*para*-Tolyl Phosphorothioate (3a) [4143-38-8]

To a stirred solution of sulfonylhydrazide **2a** (1.2 mmol) in 1,4-dioxane (2 mL) were added diethyl H-phosphonate, **1a** (1.0 mmol) and CuI (10 mol%) successively. The resulting reaction mixture was heated at the 80 °C for 4 h. Subsequently, the reaction mixture was allowed to reach ambient temperature, and the solvent was evaporated to furnish a residue which was purified by silica gel chromatography, eluting with hexane/ethyl acetate (10:1 to 2:1) to afford the phosphorothioate **3a** as a yellow liquid; yield: 2.29 g (88%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.44$ (d, $J = 7.7$ Hz, 2H), 7.16 (d, $J = 7.7$ Hz, 2H), 4.29–4.10 (m, 4H), 2.35 (s, 3H), 1.31 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 139.2 (d, $J = 2.7$ Hz), 134.5 (d, $J = 4.9$ Hz), 130.1, 122.7 (d, $J = 7.1$ Hz), 63.9 (d, $J = 6.0$ Hz), 21.1, 16.0 (d, $J = 7.1$ Hz); ^{31}P NMR (200 MHz, $CDCl_3$): $\delta = 23.4$; IR (neat): $\nu = 2999$, 2908, 1712, 1247 (P=O), 1215, 1012, 744 cm^{-1}; HR-MS: $m/z = 261.0706$, calculated for $C_{11}H_{17}O_3PS$ (M+H): 261.0708.

Scaled-Up Reaction of 3a

To a stirred solution of sulfonylhydrazide **2a** (24.0 mmol) in 1,4-dioxane (60 mL) were added diethyl H-phosphonate, **1a** (20.0 mmol) and CuI (10 mol%) successively. The resulting reaction mixture was heated at the 80 °C for 12 h. Subsequently, the reaction mixture was allowed to reach ambient temperature, and the solvent was evaporated to afford a residue which was purified by silica gel chromatography, eluting with hexane/ethyl acetate (10:1 to 2:1) furnishing the phosphorothioate **3a** as yellow liquid; yield: 45.8 g (88%).

The following *S*-aryl/alkyl phosphorothioate compounds were generated employing 1 mmol of phosphorus compound, 1.2 mmol of aryl/alkylsulfonylhydrazide and 0.1 mmol of CuI in dioxane under heating at 80 °C for 4 h in the open air.

***O,O*-Diethyl *S*-phenyl phosphorothioate (3b) [1889-58-3]:** Yellow liquid; yield: 211 mg (86%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.59$–7.55 (m, 2H), 7.38–7.32 (m, 3H), 4.29–410 (m, 4H), 1.31 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 134.5$ (d, $J = 4.5$ Hz), 129.3, 129.0, 64.0 (d, $J =$ 6.6 Hz), 16.0 (d, $J = 6.6$ Hz); ^{31}P NMR (200 MHz, $CDCl_3$): $\delta = 22.8$; IR (neat): $\nu = 3482$, 2984, 2925, 2853, 1644, 1581, 1475, 1441, 1247 (P=O), 1161, 1007, 970, 746 cm^{-1}; HR-MS: $m/z = 247.0549$, calculated for $C_{10}H_{15}O_3PS$ (M+H): 247.0552.

***O,O*-Dimethyl *S*-*para*-tolyl phosphorothioate (3c) [93116-00-8]:** Yellow liquid; yield: 197.2 mg (85%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.44$ (dd, $J = 8.3$ Hz, $J = 2.3$ Hz, 2H), 7.17 (d, $J = 8.3$ Hz), 3.84 (s, 3H), 3.80 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 139.4$ (d, $J = 2.7$ Hz), 134.5 (d, $J = 5.5$ Hz), 131.1 (d, $J = 1.8$ Hz), 128.4, 128.1, 122.0 (d, $J = 7.3$ Hz), 54.0 (d, $J = 5.5$ Hz), 21.0; ^{31}P NMR (200 MHz, $CDCl_3$): $\delta = 26.7$; IR (neat): $\nu = 3019$, 2921, 1725, 1492, 1257 (P=O), 1215, 1018, 757 cm^{-1}; HR-MS: $m/z = 233.0394$, calculated for $C_9H_{13}O_3PS$ (M+H): 233.0395.

***O,O*-Diisopropyl *S*-*para*-tolyl phosphorothioate (3d) [145586-66-9]:** Yellow liquid; yield: 242 mg (84%); ^{1}H NMR

(300 MHz, $CDCl_3$): $\delta = 7.47$ (dd, $J = 8.3$ Hz, $J = 2.3$ Hz, 2H), 7.14 (d, $J = 8.3$ Hz, 2H), 4.87–4.68 (m, 2H), 2.34 (s, 3H), 1.33 (d, $J = 6.0$ Hz, 6H), 1.26 (d, $J = 6.0$ Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 138.7$ (d, $J = 2.7$ Hz), 134.1 (d, $J = 4.5$ Hz), 129.8 (d, $J = 1.8$ Hz), 123.1 (d, $J = 6.4$ Hz), 73.0 (d, $J = 7.3$ Hz), 23.6 (d, $J = 4.5$ Hz), 23.4 (d, $J = 5.5$ Hz), 21.0; ^{31}P NMR (200 MHz, $CDCl_3$): $\delta = 20.9$; IR (neat): $\nu = 2979$, 2927, 1729,1689, 1492, 1252 (P=O), 979, 768 cm^{-1}; HR-MS: $m/z = 289.1019$, calculated for $C_{13}H_{21}O_3PS$ (M+H): 289.1021.

***S*-2,5-Dimethylphenyl *O,O*-diethyl phosphorothioate (3e):** Yellow liquid; yield: 230 mg (84%); ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.41$ (s, 1H), 7.18–7.01 (m, 2H), 4.23–4.08 (m, 4H), 2.47 (s, 3H), 2.30 (s, 3H), 1.35–1.24 (m 6H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 138.9$ (d, $J = 5.4$ Hz), 136.6 (d, $J = 4.5$ Hz), 136.1 (d, $J = 2.7$ Hz), 130.5 (d, $J = 2.7$ Hz), 130.2 (d, $J = 2.7$ Hz), 124.9 (d, $J = 7.3$ Hz), 63.9 (d, $J = 7.3$ Hz), 20.7, 20.5, 16.0 (d, $J = 7.3$ Hz); ^{31}P NMR (200 MHz, $CDCl_3$): $\delta = 23.3$; IR (neat): $\nu = 2981$, 2923, 1738, 1490, 1253 (P=O), 1215, 1014, 971, 750 cm^{-1}; HR-MS: $m/z = 275.0860$, calculated for $C_{12}H_{19}O_3PS$ (M+H): 275.0865.

***O,O*-Diethyl *S*-mesityl phosphorothioate (3f):** Yellow liquid; yield: 245 mg (85%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.94$ (s, 2H), 4.17–4.04 (m, 4H), 2.53 (d, $J = 1.5$ Hz, 6H), 2.25 (d, $J = 2.4$ Hz, 3H), 1.29 (dt, $J = 7.1$ Hz, $J = 0.8$ Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 143.9$ (d, $J = 5.4$ Hz), 139.4 (d, $J = 4.5$ Hz), 129.4 (d, $J = 2.7$ Hz), 122.2 (d, $J = 8.2$ Hz), 64.1 (d, $J = 7.3$ Hz), 22.4, 20.1, 16.0 (d, $J = 7.3$ Hz); ^{31}P NMR (200 MHz, $CDCl_3$): $\delta = 23.6$; IR (neat): $\nu = 3743$, 3396, 2981, 2923, 2853, 1601, 1550, 1443, 1247 (P=O), 1162, 1012, 966, 771, 603 , cm^{-1}; HR-MS: $m/z = 289.1017$, calculated for $C_{13}H_{21}O_3PS$ (M+H): 289.1021.

***O,O*-Diethyl *S*-naphthalen-2-yl phosphorothioate (3g) [109161-61-7]:** Yellow liquid; yield: 225 mg (76%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.53$ (d, $J = 8.3$ Hz, 1H), 7.92–7.84 (m, 3H), 7.64–7.43 (m, 3H), 4.22–4.03 (m, 4H), 1.21–1.16 (dt, $J = 7.0$ Hz, $J = 0.7$ Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 135.2$ (d, $J = 5.5$ Hz), 134.6, 134.2, 130.3 (d, $J = 3.3$ Hz), 128.5, 127.0, 126.4, 125.8, 125.6 (d, $J = 2.7$ Hz), 64.2 (d, $J = 6.6$ Hz), 15.9 (d, $J = 7.1$ Hz); ^{31}P NMR (200 MHz, $CDCl_3$): $\delta = 22.7$; IR (neat): $\nu = 3743$, 3610, 3056, 2984, 2906, 1741, 1502, 1254 (P=O), 1014, 772 , cm^{-1}; HR-MS; $m/z = 297.0705$, calculated for $C_{14}H_{17}O_3PS$ (M+H): 297.0708.

***S*-4-Chlorophenyl *O,O*-diethyl phosphorothioate (3h) [4524-70-3]:** Yellow liquid; yield: 241 mg (86%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.49$ (dd, $J = 8.5$ Hz, $J = 1.9$ Hz, 2H), 7.31 (d, $J = 8.5$ Hz, 2H), 4.27–4.08 (m, 4H), 1.30 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 135.7$ (d, $J = 4.5$ Hz), 135.5 (d, $J = 3.6$ Hz), 129.5, 125.1 (d, $J = 7.3$ Hz), 64.2 (d, $J = 6.4$ Hz), 16.0 (d, $J = 6.4$ Hz); ^{31}P NMR (200 MHz, $CDCl_3$): $\delta = 22.2$; IR (neat): $\nu = 3484$, 2983, 2923, 2852, 1728, 1475, 1390, 1253 (P=O), 1009, 973, 772 cm^{-1}; HR-MS: $m/z = 281.0158$, calculated for $C_{10}H_{14}O_3ClPS$ (M+H): 281.0162.

***S*-2-Chloro-4-methylphenyl *O,O*-diethyl phosphorothioate (3i):** Yellow liquid; yield: 232 mg (79%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.54$ (dd, $J = 8.3$ Hz, $J = 2.3$ Hz, 1H), 7.26 (s, 1H), 7.16 (dd, $J = 8.3$ Hz, $J = 2.3$ Hz, 1H), 4.26–4.07 (m, 4H), 2.50 (s, 3H), 1.31 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 144.0$ (d, $J = 5.5$ Hz), 137.3 (d, $J = 3.8$ Hz), 135.4 (d, $J = 3.8$ Hz), 130.7 (d, $J = 2.2$ Hz), 126.9 (d, $J = 2.2$ Hz), 124.3 (d, $J = 7.2$ Hz), 64.3 (d, $J = 6.6$ Hz), 21.3, 16.0 (d, $J = 7.2$ Hz); ^{31}P NMR (200 MHz, $CDCl_3$): $\delta = 22.5$; IR (neat): $\nu = 3445$, 2976, 2834, 1732, 1467, 1387, 1242 (P=O), 1013, 976, 765 cm^{-1}; HR-MS: $m/z = 295.0317$, calculated for $C_{11}H_{16}O_3ClPS$ (M+H): 295.0319.

***S*-4-Bromophenyl *O,O*-diethyl phosphorothioate (3j) [15224-36-9]:** Yellow liquid; yield: 279 mg (86%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.50$–7.41 (m, 4H), 4.29–4.10 (m, 4H), 1.32 (t, $J = 6.8$ Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 135.9$ (d, $J = 5.5$ Hz), 132.4 (d, $J = 1.8$ Hz), 125.7 (d, $J = 6.4$ Hz), 123.6 (d, $J = 2.7$ Hz), 64.2 (d, $J = 6.4$ Hz), 16.0 (d, $J = 7.3$ Hz); ^{31}P NMR (200 MHz, $CDCl_3$): $\delta = 21.9$; IR (neat): $\nu = 3744$, 3610, 2922, 2851, 1709, 1472, 1389, 1255 (P=O), 1219, 1009, 974, 772 cm^{-1}; HR-MS: $m/z = 346.9467$, calculated for $C_{10}H_{14}O_3BrPS$ (M+Na): 346.9477.

***O,O*-Diethyl *S*-2-fluoro-5-methylphenyl phosphorothioate (3k):** Yellow liquid; yield: 234 mg (84%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.41$–7.34 (m, 1H), 7.24–7.19 (m, 1H), 7.04–6.94 (m, 1H) 4.29–4.09 (m, 4H), 2.47 (s, 3H) 1.31 (t, $J = 6.8$ Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 160.4$ (d, $J = 247.0$ Hz), 137.5 (d, $J = 13.6$ Hz), 131.5 (d, $J = 5.4$ Hz), 127.0 (t, $J = 7.3$ Hz), 122.2 (d, $J = 22.7$ Hz), 116.2 (d, $J = 19.9$ Hz), 64.2 (d, $J = 6.4$ Hz), 20.3, 15.8 (d, $J = 6.4$ Hz); ^{31}P NMR (200 MHz, $CDCl_3$): $\delta = 22.1$; IR (neat): $\nu = 3765$, 3018, 2987, 1487, 1214 (P=O), 1009, 974, 742 cm^{-1}; HR-MS: $m/z = 279.0611$, calculated for $C_{11}H_{16}FO_3PS$ (M+H): 279.0615.

***O,O*-Diethyl *S*-2-methyl-5-nitrophenyl phosphorothioate (3l):** Yellow liquid; yield: 256 mg (84%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.49$ (t, $J = 2.3$ Hz, 1H), 8.13 (m, 1H), 7.43 (d, $J = 8.3$ Hz, 1H), 4.27–4.14 (m, 4H), 2.61 (s, 3H), 1.33 (t, $J = 8.3$ Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 149.5$ (d, $J = 5.5$ Hz), 145.7, 130.9 (d, $J = 1.1$ Hz), 130.0 (d, $J = 3.8$ Hz), 127.6 (d, $J = 7.1$ Hz), 123.4 (d, $J = 1.6$ Hz), 64.1 (d, $J = 6.6$ Hz), 21.1, 15.4 (d, $J = 7.1$ Hz); ^{31}P NMR (200 MHz, $CDCl_3$): $\delta = 21.0$; IR (neat): $\nu = 2984$, 2923, 2852, 1580, 1520, 1470, 1346, 1256(P=O), 1161, 1010, 974, 771, 739 cm^{-1}; HR-MS: $m/z = 306.0556$, calculated for $C_{11}H_{16}NO_5S$ (M+H): 306.0557.

3-(Diethoxyphosphorylthio)benzoic acid (3m) [103647-17-2]: White solid; yield: 217 mg (75%), mp 110–112 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.16$ (d, $J = 15.9$ Hz 1H), 8.02 (d, $J = 7.7$ Hz, 1H), 7.88 (d, $J = 7.7$ Hz, 1H), 7.76–7.66 (m, 1H), 7.49–7.39 (m, 1H), 4.24–4.04 (m, 4H), 1.31(t, J=6.8 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 165.9$ (d, $J = 2.7$ Hz), 137.4 (dd, $J = 10.9$ Hz, $J = 4.5$ Hz), 135.8, 134.6 (d, $J = 5.4$ Hz), 131.3 (d, $J = 1.8$ Hz), 131.1, 130.3 (d, $J = 11.8$ Hz), 129.2 (m), 128.3 (m), 125.9 (d, $J = 7.3$ Hz), 63.2 (d, $J = 6.4$ Hz), 62.4, 15.0; ^{31}P NMR (200 MHz, $CDCl_3$): $\delta = 26.3$; IR (neat): $\nu = 3331$, 2945, 2833, 1704, 1660, 1450, 1415, 1219 (P=O), 1112, 1017, 772 cm^{-1}; HR-MS: $m/z = 313.0261$, calculated for $C_{11}H_{14}O_5NaPS$ (M+H): 313.0270.

***S,S'*-1,3-Phenylene *O,O,O',O'*-tetraethyl diphosphorothioate (3n) [109592-17-8]:** Yellow liquid; yield: 232 mg (56%); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.78$–7.21 (m, 4H), 4.27–4.09 (m, 8H), 1.35–1.26 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 139.8$, 137.9, 134.9, 133.2, 132.6, 130.0, 129.8, 128.1, 127.7, 125.8, 125.0, 64.2 (dd, $J = 9.1$ Hz, $J = 6.4$ Hz), 16.0 (d, $J = 7.3$ Hz); ^{31}P NMR (200 MHz, $CDCl_3$): $\delta = 22.0$ (d, $J = 22.4$ Hz); IR (neat): $\nu = 2983$, 2907, 1729, 1566, 1459, 1255 (P=O), 1012, 772 cm^{-1}; HR-MS: $m/z = 437.0373$, calculated for $C_{14}H_{23}O_6NaP_2S_2$ (M+H): 437.0382.

***O,O*-Diethyl *S*-methyl phosphorothioate (3o) [2404-05-9]:** Yellow liquid; yield: 144 mg (78%); ^{1}H NMR (300 MHz,

$CDCl_3$): $\delta = 4.28–4.09$ (m, 4H), 2.31–2.26 (d, $J = 15.1$ Hz, 3H), 1.38 (t, $J = 6.8$ Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 63.5$ (d, $J = 5.5$ Hz), 16.0 (d, $J = 7.2$ Hz), 12.3 (d, $J = 4.4$ Hz); ^{31}P NMR (200 MHz, $CDCl_3$): $\delta = 28.6$; IR (neat): $\nu = 2983$, 2932, 1741, 1644, 1442, 1245 (P=O), 1007, 957, 754 , cm^{-1}; HR-MS: $m/z = 207.0213$, calculated for $C_5H_{13}O_3PS$ (M + Na): 207.0215.

***S*-Butyl *O,O*-diethyl phosphorothioate (3p) [20195-07-7]:** Yellow liquid; yield: 194 mg (86%); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 4.26–4.07$ (m, 4H), 2.84 (m, 2H), 1.72–1.62 (m, 2H), 1.49–1.39 (m, 2H), 1.37 (t, $J = 6.8$ Hz, 6H), 0.93 (t, $J = 7.6$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 63.4$ (d, $J = 5.5$ Hz), 32.7 (d, $J = 5.5$ Hz), 30.5 (d, $J = 4.5$ Hz), 21.6, 16.0 (d, $J = 7.3$ Hz), 13.4; ^{31}P NMR (200 MHz, $CDCl_3$): $\delta = 21.4$; IR (neat): $\nu = 3747$, 2957, 2921, 2852, 1509, 1461, 1219 (P=O), 967, 772 cm^{-1}; HR-MS: $m/z = 227.0865$, calculated for $C_8H_{19}O_3PS$ (M + H): 227.0865.

***S*-Benzyl *O,O*-diethyl phosphorothioate (3q) [13286-32-3]:** Yellow liquid; yield: 224 mg (86%); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.36–7.24$ (m, 5H), 4.15–3.98 (m, 6H), 1.28 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 137.4$ (d, $J = 5.5$ Hz), 128.8, 128.5, 127.5, 63.4 (d, $J = 5.5$ Hz), 34.8, 15.8 (d, $J = 6.4$ Hz); ^{31}P NMR (200 MHz, $CDCl_3$): $\delta = 26.7$; IR (neat): $\nu = 3482$, 2984, 2922, 2843, 1654, 1581, 1445, 1421, 1223 (P=O), 1141, 1017, 970, 746 cm^{-1}; HR-MS: $m/z =$ 261.0706, calculated for $C_{11}H_{17}O_3PS$: 261.0709.

***S*-(7,7-Dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methyl *O,O*-diethyl phosphorothioate (3r):** Yellow liquid; yield: 275 mg (86%), $[\alpha]_D^{25}$: 9 (*c* 1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 4.28–4.09$ (m, 4H), 2.31–2.26 (d, $J = 15.1$ Hz, 3H), 1.38 (t, $J = 6.8$ Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 216.7$, 63.6 (d, $J = 5.9$ Hz), 60.4 (d, $J = 5.9$ Hz), 43.7, 43.0, 29.7, 26.9, 22.7, 21.1, 19.8, 16.0 (d, $J = 8.8$ Hz), 14.2 (d, $J = 5.9$ Hz); ^{31}P NMR (200 MHz, $CDCl_3$): $\delta = 28.5$; IR (neat): $\nu = 3744$, 3610, 2959, 2917, 2849, 1741, 1514, 1245 (P=O), 1218, 1017, 754 cm^{-1}; HR-MS: $m/z = 321.1282$, calculated for $C_{14}H_{25}O_4PS$ (M + H): 321.1289.

***S-para*-Tolyl diphenylphosphinothioate (3s) [5510-81-6]:** White solid; yield: 279 mg (86%); mp 112–113 °C; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.87–7.83$ (m, 4H), 7.53–7.42 (m, 6H), 7.32 (d, $J = 7.8$ Hz, 2H), 7.01 (d, $J = 7.8$ Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 139.1$ (d, $J = 2.2$ Hz), 135.3 (d, $J = 3.9$ Hz), 133.1 (d, $J = 7.2$ Hz), 132.2 (d, $J = 2.8$ Hz), 131.6 (d, $J = 10.5$ Hz), 129.9 (d, $J = 1.7$ Hz), 128.4 (d, $J = 13.2$ Hz), 122.0 (d, $J = 5.0$ Hz), 21.1; ^{31}P NMR (200 MHz, $CDCl_3$): $\delta = 41.9$; IR (neat): $\nu = 3056$, 3021, 2922, 2852, 1720, 1490, 1437, 1203 (P=O), 1114, 808, 750, 724, 695 cm^{-1}; HR-MS: $m/z = 325.0809$, calculated for $C_{19}H_{17}OPS$ (M + H): 325.0810.

***S-para*-Tolyl bis(3-methoxyphenyl)phosphinothioate (3t):** White solid; yield: 326 mg (85%), mp: 146–148 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.59–7.33$ (m, 8H), 7.05–7.02 (m, 4H), 3.80 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 139.2$ (d, $J = 2.7$ Hz), 135.4 (d, $J = 3.9$ Hz), 133.1, 130.0 (d, $J = 2.2$ Hz), 129.7, 129.5, 128.5 128.3 123.7, 123.8, 118.8 (d, $J = 2.8$ Hz), 116.2, 116.1, 55.4, 21.1; ^{31}P NMR (200 MHz, $CDCl_3$): $\delta = 41.8$; IR (neat): $\nu = 3749$, 3610, 2923, 2852, 1591, 1481, 1420, 1250 (P=O), 1201, 1183, 1038, 781, 692 , cm^{-1}; HR-MS: $m/z = 385.1010$, calculated for $C_{21}H_{21}O_3PS$ (M + H): 385.1027.

***S-para*-Tolyl dibutylphosphinothioate (3u):** Yellow liquid; yield: 239 mg (84%); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.46$ (d, $J = 7.9$ Hz, 2H), 7.17 (d, $J = 7.9$ Hz, 2H), 2.35 (s, 3H), 1.93–1.83 (m, 4H), 1.73–1.51 (m, 6H), 0.95–0.87 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 139.3$ (d, $J = 1.8$ Hz), 135.4 (d, $J = 3.6$ Hz), 130.2 128.5 31.2, 30.6, 24.4 (d, $J = 3.6$ Hz), 23.9, 23.8, 21.2, 13.6; ^{31}P NMR (200 MHz, $CDCl_3$): $\delta = 59.3$; IR (neat): $\nu = 3727$, 2957, 2931, 2854, 1513, 1461, 1243 (P=O), 974, 778 cm^{-1}; HR-MS: $m/z = 285.1434$, calculated for $C_{15}H_{27}OPS$ (M + H): 285.1436.

***S-para*-Tolyl *tert*-butyl(phenyl)phosphinothioate (3v):** Yellow liquid; yield: 258 mg (85%); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.88–7.84$ (m, 2H), 7.47–7.33 (m, 5H), 6.96 (d, $J = 7.9$ Hz, 2H), 2.20 (s, 3H), 1.23 (d, $J = 16.9$ Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 139.3$, 135.4 (d, $J = 2.7$ Hz) 133.0 (d, $J = 9.1$ Hz) 131.7 (d, $J = 2.7$ Hz), 130.3, 129.7, 128.7 (d, $J = 11.8$ Hz), 127.8 (d, $J = 11.8$ Hz), 121.8 (d, $J = 5.4$ Hz), 29.5, 24.8, 20.9; ^{31}P NMR (200 MHz, $CDCl_3$): $\delta = 55.4$; IR (neat): $\nu = 2957$, 2921, 2852, 1515, 1463, 1216 (P=O), 1166, 909, 771 cm^{-1}; HR-MS: $m/z = 305.1122$, calculated for-$C_{17}H_{21}OPS$ (M + H): 305.1124.

***O*-Ethyl *S-para*-tolyl phenylphosphonothioate (3w) [681460-69-5]:** Yellow liquid; yield: 248 mg (85%);^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.68–7.63$ (m, 2H), 7.51–7.47 (m, 1H), 7.38–7.34 (m, 2H), 7.16 (dd, $J = 7.9$ Hz, $J = 1.5$ Hz, 2H), 7.01 (d, $J = 7.9$ Hz, 2H), 4.40–4.28 (m, 2H), 2.28 (s, 3H), 1.39 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 139.1$ (d, $J = 2.7$ Hz), 135.3 (d, $J = 3.6$ Hz), 132.3 (d, $J = 2.7$ Hz), 131.3 (d, $J = 10.9$ Hz), 129.8 (d, $J = 1.8$ Hz), 128.1, 128.0, 122.6 (d, $J = 6.4$ Hz), 62.3 (d, $J = 6.4$ Hz), 21.0 16.2 (d, $J = 6.4$ Hz); ^{31}P NMR (200 MHz, $CDCl_3$): $\delta = 42.4$; IR (neat): $\nu = 3476$, 2922, 1592, 1439, 1232 (P=O), 1118, 1018, 953, 749 , cm^{-1}; HR-MS: $m/z = 293.0754$, calculated for $C_{15}H_{17}O_2PS$ (M + H): 293.0759.

***O*-(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl *S-para*-tolyl phenylphosphonothioate (3x):** Yellow liquid; yield: 342 mg (85%); $[\alpha]_D^{25}$: 74 (*c* 1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.74–7.66$ (m, 2H), 7.52–7.34 (m, 3H), 7.25–7.21 (m, 2H), 7.03–6.99 (m, 2H), 4.56–4.41 (m, 1H), 2.28 (s, 3H), 1.75–1.33 (m, 5H), 1.29–1.18 (m, 2H), 0.96–0.80 (m, 11H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 138.9$, 135.3, 132.1, 131.4, 129.8, 128.2, 128.0, 79.8 (d, $J = 8.8$ Hz), 48.7 (d, $J = 6.6$ Hz), 43.3 (d, $J = 7.2$ Hz), 34.0, 31.6 (d, $J = 2.7$ Hz), 29.7, 25.6, 22.9 (d, $J = 4.9$ Hz), 22.0 (d, $J = 10.5$ Hz), 21.1 (d, $J = 16.0$ Hz), 16.0; ^{31}P NMR (200 MHz, $CDCl_3$): $\delta = 39.9$, 40.2; IR (neat): $\nu = 3052$, 2953, 2923, 2867, 1898, 1727, 1491, 1454, 1235 (P=O), 1117, 978, 807, 714, 692 cm^{-1}; HR-MS: $m/z = 403.1858$, calculated for $C_{23}H_{31}O_2PS$ (M + H): 403.1855.

Diphenyl(*p*-tolylthio)phosphine·borane (3y): Yellow liquid; yield: 274 mg (85%); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.91–7.87$ (m, 4H), 7.56–7.46 (m, 6H), 7.36 (d, $J = 7.9$ Hz, 2H), 7.04 (d, $J = 7.9$ Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 139.1$, 135.2 (d, $J = 4.4$ Hz), 132.2 (d, $J = 4.4$ Hz), 131.6, 131.5, 129.9, 128.5, 128.3, 21.1; ^{31}P NMR (200 MHz, $CDCl_3$): $\delta = 41.5$; IR (neat): $\nu = 3056$, 2921, 2852, 1726, 1490, 1437, 1200 (P=O), 1114, 1071, 808, 750, 694 cm^{-1}; HR-MS: $m/z = 325.0781$, calculated for $C_{19}H_{20}BPS$: 322.1116.

***S*-Phenyl *tert*-butyl(phenyl)phosphinothioate (3z):** Yellow liquid; yield: 235 mg (81%); ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.88–7.83$ (m, 2H), 7.48–7.44 (m, 5H), 7.20–7.14 (m, 3H), 1.24 (d, $J = 16.9$ Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 139.2$, 135.3 (d, $J = 3.6$ Hz) 133.1 (d, $J = 9.1$ Hz) 131.8 (d, $J = 1.8$ Hz), 128.9, 128.5, 128.0 (d, $J = 11.8$ Hz), 125.9 (d, $J =$

5.4 Hz), 29.6, 24.9; ^{31}P NMR (200 MHz, $CDCl_3$): $\delta = 65.2$; IR (neat): $\nu = 2962$, 2928, 2912, 1531, 1483, 1246 (P=O), 1166, 909, 771 cm^{-1}; HR-MS: m/z291.0969, calculated for $C_{16}H_{19}OPS$ (M+H): 291.0968.

Supporting Information

Full experimental details along with copies of ^{1}H, ^{13}C and ^{31}P NMR spectra of all compounds are available in the Supporting Information.

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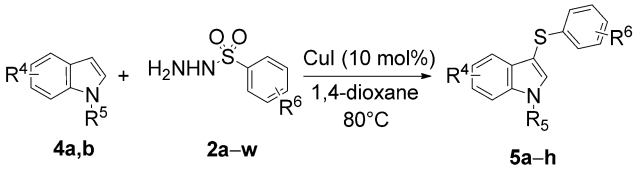
[14] A range of substituted indoles was successfully sulfenylated with various arylsulfonylhydrazides in the presence of 10 mol% of CuI in dioxane at 80 °C (see the Supporting Information).



4a,b **2a–w** **5a–h**

[15] The diastereomeric ratio of the starting material **2x** was found to be 60:40 and the same was subjected to sulfenylation.

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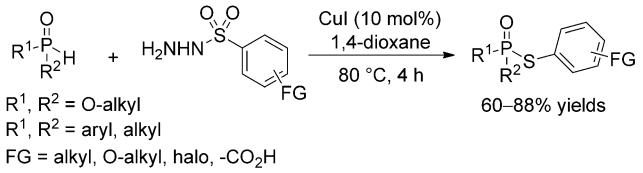
Copper(I)-Induced Sulfenylation of H-Phosphonates, H-Phosphonites and Phosphine Oxides with Aryl/alkylsulfonylhydrazides as a Thiol Surrogate

Adv. Synth. Catal. **2014**, *356*, 1 – 9

Gullapalli Kumaraswamy,* Ragam Raju



R^1, R^2 = O-alkyl
R^1, R^2 = aryl, alkyl
FG = alkyl, O-alkyl, halo, -CO_2H

9

