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Metal- and Oxidant-Free S–P(O) Bond Construction via Direct Coupling of P(O)H with Sulfinic Acids

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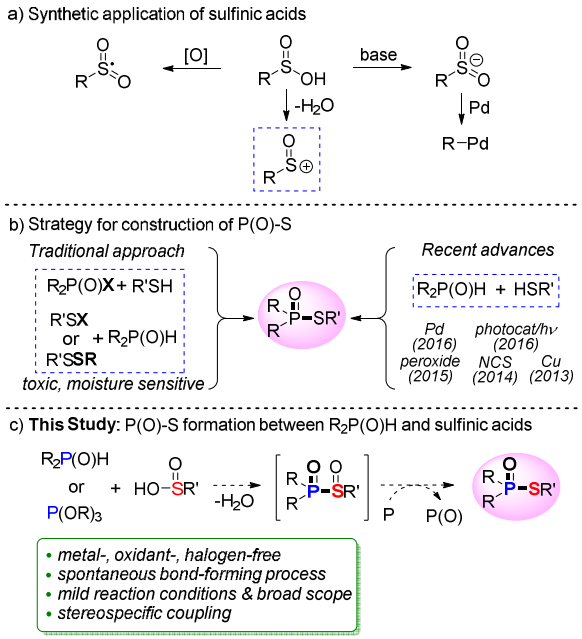
We have developed a simple and convenient method for S–P(O) bond formation between $R_2P(O)H$ and sulfinic acids under metal-, oxidant-, and halogen-free conditions. The current method is compatible with a broad range of substituents on various substrates including halogens and heterocyclic moieties. The synthetic potential of this method was further highlighted by the expeditious synthesis of optically active *P*-chiral phosphorothioates via stereospecific coupling.

Introduction

The S–P(O) structural motif is a versatile and important building block that is widely present in biologically active molecules including pesticides, insecticides, enzyme inhibitors, and pharmaceuticals.[1] Therefore, the significance of thiophosphates has inspired chemists to develop efficient and selective methods for S–P(O) bond-formation. The traditional synthetic approach to S–P(O) bond formation is based on nucleophilic substitution using $R_2P(O)X$ or RSX.[2] However, extensive applications of traditional protocols often suffer from limitations in the preparation of toxic and moisture-sensitive P- or S-reactants, poor functional group tolerance or harsh reaction conditions. To overcome these challenges, considerable efforts have been made in the direct cross-coupling reactions of H-phosphine oxides/H–phosphinates with thiols.[3-5] Recently, peroxide or *N*-chlorosuccinimide-mediated reactions have been successfully applied to activate thiols for S–P(O) bond formation.[4] Furthermore, impressive results were obtained by using Pd-catalyzed coupling reactions[3a] or photocatalysis[5] to produce phosphorothioate derivatives. As these methods require expensive transition metal catalysts, oxidants, or foul smelling thiols, an alternative strategy to generate this moiety via a simple and environmentally benign protocol is still in great demand.

In this context, we were intrigued by developing a new method for S–P(O) bond formation without using any metals or oxidants in the reaction. It is well known that sulfinic acids are versatile compounds that are widely used in a variety of reactions via the formation of either sulfonyl anion[6,7] or radical reactive species[8] (Scheme 1a). In addition, Pd-catalyzed desulfitative/cross-coupling reactions using sulfinate derivatives as coupling partners have been used for C–C bond formation reactions.[9] On the other hand, reactions with sulfinyl cations from sulfinic acids have rarely been described in the literature except for sulfenylation with indoles.[10] We questioned whether the sulfinyl cations generated from sulfinic acids could be suitable coupling partners for the P(O)H moiety with high efficiency. We speculated that if sulfinylphosphine oxide generated in situ as a result of cross coupling of a sulfinyl cation and H-phosphoryl compounds, it could be further converted to the phosphorothioate moiety via concomitant reduction (Scheme 1c). Notably, this new approach differs from other S–P(O) bond formation methods in which thiols are typically oxidized for the preparation of sulfide precursors



Scheme 1 Synthetic application of sulfinic acids and strategies for S-P(O) bond formation.

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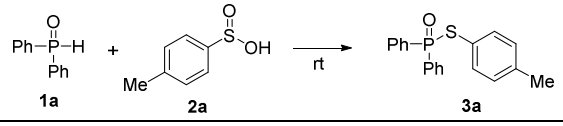
during the coupling reaction process. Herein, we present a novel and powerful strategy for S–P(O) bond formation that is enabled by the direct cross coupling of H-phosphoryl compounds and sulfinic acids under metal- and oxidant-free conditions.

Results and discussion

In line with our hypothesis, the feasibility of this strategy relies on the initial coupling process of two reactants, and we explored the coupling reaction of H-phosphine oxide **1a** with sulfinic acid **2a** (Table 1). To our delight, our initial investigations revealed that **1a** and **2a** reacted smoothly to afford desired product **3a** in 44% yield in toluene at room temperature, thus demonstrating that the overall process occurred spontaneously (Table 1, entry 1). The intermediate sulfinylphosphine oxide was not detected during the reactions, and a significant amount of diphenylphosphinic acid was isolated, which was likely due to diphenylphosphine oxide **1a** also acting as a reductant during the process. Therefore, we sought an alternative set of reaction conditions that would be capable of overcoming this problem. The experiments indicated that the reaction efficacy was promoted by addition of arylphosphine,[11] and the yield improved to 72% using triphenylphosphine with only a negligible amount of diphenylphosphinic acid by-product (entry 6). An excess of sulfinic acid (2 equiv) was needed to ensure complete conversion of **1a**. After extensive screenings, the optimal parameters were determined and involved additive free conditions at room temperature for 24 h. Interestingly, less toxic isopropyl acetate and *t*-butyl acetate exhibited the best reactivity in the solvent screening (entries 7 and 10). Notably, further increasing the reaction temperature to 40 °C did not provide any significant changes in the yield of the product (Table 1, entry 8). The use of the preformed sodium sulfinate salt of **2a** as a starting material did not react with H-phosphine oxide **1a** (Table 1, entry 11).

Table 1 Optimization of coupling of diphenylphosphine oxide **1a** with 4-methylbenzene sulfinic acid **2a**.[a]

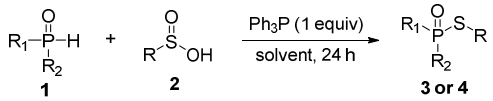


Entry	Additive [1 equiv]	Solvent	Yield [%][b]
1	-	PhMe	44
2	pyridine	PhMe	42
3	Cy_3P	PhMe	trace
4	$(C_6F_5)_3P$	PhMe	51
5	$(4\text{-MeOPh})_3P$	PhMe	69
6	Ph_3P	PhMe	72
7	Ph_3P	*i*-PrOAc	86
8[c]	Ph_3P	*i*-PrOAc	83
9	Ph_3P	MeCN	62
10	Ph_3P	*t*-BuOAc	82
11[d]	Ph_3P	*i*-PrOAc	trace

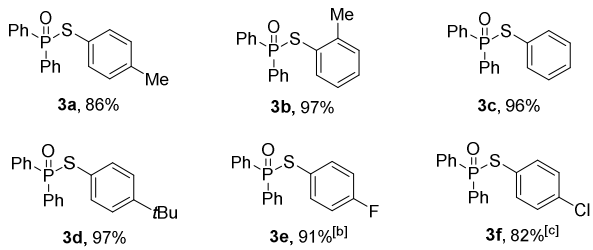
[a] Reaction conditions: **1a** (0.17 mmol), **2a** (2.0 equiv), additive (1.0 equiv), and solvent (1.0 mL) under N_2 at room temperature for 24 h. [b] isolation yield. [c] Reacted at 40 °C. [d] Sodium sulfinate was used instead of **2a**.

With the optimized reaction conditions in hand, the scope of the reaction was studied with respect to both sulfinic acids and H-phosphoryl compounds (Table 2). The substituted arylsulfinic acids bearing methyl, *tert*-butyl, and methoxy on the aryl ring reacted well with H-phosphine oxide to afford the desired coupling products in good yields (**3a-3d, 3k**). It is important to note that the halo substituents including I, Br, Cl, and F on the phenyl ring of the substrates (**3e-3h**) were well tolerated under the reaction conditions, enabling further functionalization at these positions. These results are significant because iodide and bromide groups on aromatic rings are typically difficult to retain in transition metal-catalyzed reactions. In a similar fashion, substrates with trifluoromethyl (-CF_3) or trifluoromethoxy (-OCF_3) groups, which are useful structural motifs in many biologically active molecules, can be employed to afford the corresponding products (**3i** and **3j**) in excellent yield. A bulkier 2-naphthylsulfinic acid substrate is also effective to afford the desired product **3l** in 86% yield. In addition, aliphatic sulfinic acids, such as isopropyl-, benzyl-, phenylethyl-, and cyclopropyl sulfinic acids, were also effective producing the desired products (**3m-3p)** in good yield. Further exploration demonstrated that heterocyclic sulfinic acids that are typically incompatible with strong oxidative conditions, as exemplified by thiophene and dihydrobenzofuran could also be used as coupling partners (**3q-3r)**. Next, the scope of this transformation with respect to the P(O)-H compounds was evaluated. A range of H-phosphonates, H-phosphinates, and phosphine oxide substrates (**4a-4r**) was determined to be suitable reaction partners for this transformation. Therefore, the current protocol can be used to synthesize phosphorothioate derivatives with substituents at various positions, providing considerable advantages in both simplicity and efficiency. In case of H-phosphonates, the addition of DBU improved the reactivity probably because the equilibrium in phosphite-phosphonate tautomerism shifts toward the reactive phosphite form under basic conditions.[12]

Table 2 Scope of the coupling reactions.[a]



Scope of sulfinic acids:



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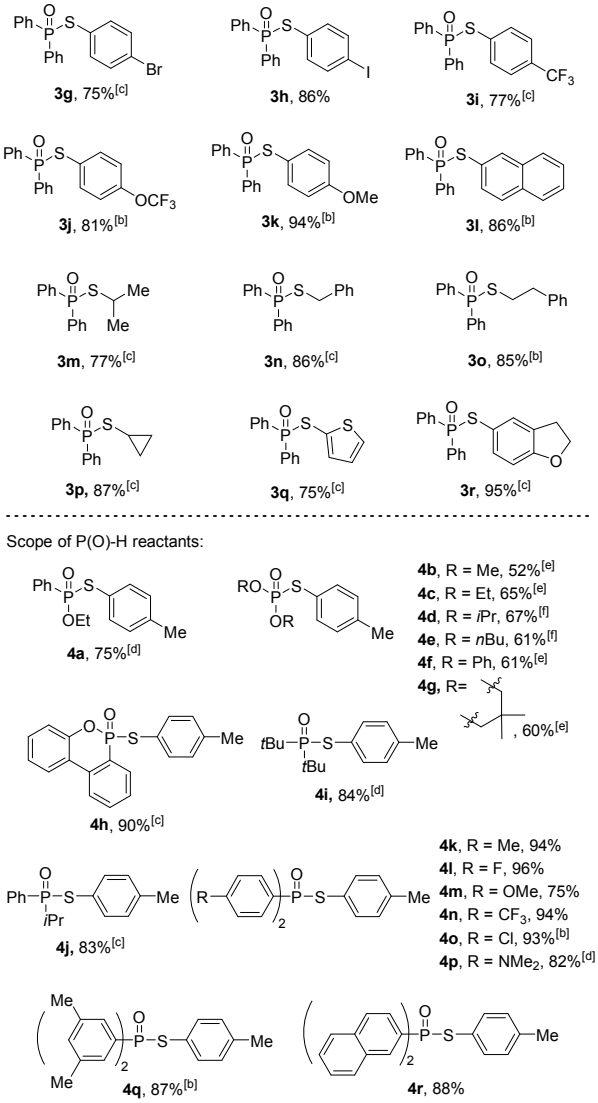
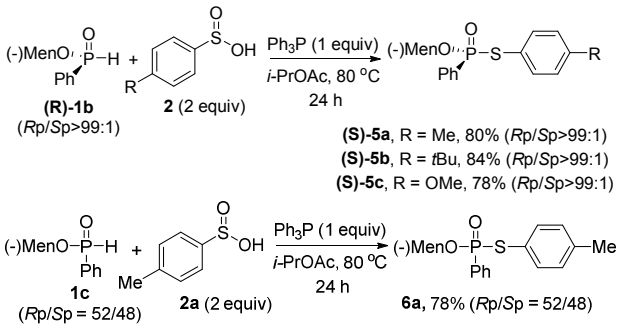


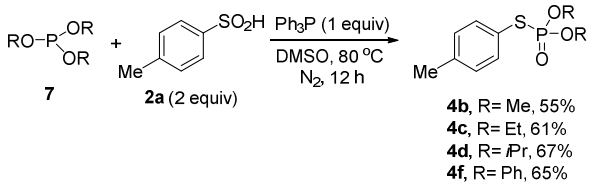
[a] Reaction conditions: **1** (1.0 equiv), **2** (2.0 equiv), and Ph_3P (1.0 equiv) under N_2 (1 atm) in *i*-PrOAc (0.17 M) at room temperature for 24 h. Isolated yields. [b] Reacted at 40 °C. [c] Reacted at 60 °C. [d] Reacted at 80 °C. [e] DBU (1.0 equiv) in MeCN (0.10 M) at 60 °C. [f] DBU (1.0 equiv) in MeCN (0.10 M) at 80 °C.

Due to the importance of optically active organophosphorus compounds as biological active compounds and chiral auxiliaries,[13] the stereochemistry on the reactions of *R*p-(–)-menthyl phenyl H-phosphinate (*R*p-**1b**, *R*p/*S*p > 99/1) with aryl sulfinic acids was investigated. To our delight, the corresponding *P*-chiral phosphorothioates were prepared stereospecifically with retention of configuration at the phosphorus centers (Scheme 2). The other diastereomer was not detected from the crude products using ^1H and ^{31}P NMR spectroscopy. Moreover, when a diastereomeric mixture of **1c** (*R*p/*S*p = 52/48) was employed, **6a** was obtained as a mixture of diastereomers with the same ratio, thus demonstrating the efficiency of this method for preparing optically active *P*-chiral phosphorothioates derivatives.



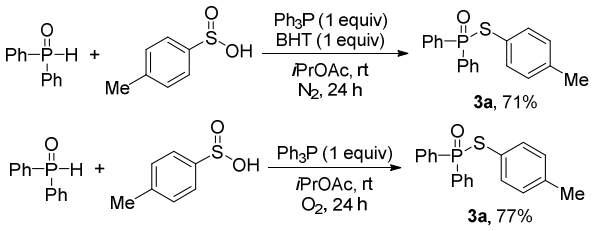
Scheme 2 Stereospecific coupling reaction for the formation of *P*-chiral phosphorothioates.

To fully evaluate this method, different H-phosphoryl compounds were investigated. Impressively, expanding the scope to various phosphite reactants was also possible, producing the coupling product (**4b-d**, **4f**) under the comparable reaction conditions (Scheme 3).



Scheme 3 Reaction of phosphites with 4-methylbenzenesulfinic acid.

To obtain mechanistic information of the reaction process, radical trapping experiments were conducted by employing 2,6-Di-*tert*-butyl-4-methylphenol (BHT) whether the reaction involves radical species. In addition, a model reaction was performed under an O_2 atmosphere because O_2 was used as a radical initiator.[8] No influence of this transformation was found, providing **3a** in 71% and 77% yields, respectively, indicating that a radical process may not be involved in the coupling reaction (scheme 4).



Scheme 4 Control experiments.

Based on the above observations and previous reports, a plausible mechanism is shown in Scheme 5. Initially, tautomerization of diphenylphosphine oxide **1a**, which is a so-called P(V) form, exists in equilibrium with the P(III) form **1a'**.[12b] The reaction pathway is likely to be triggered by the formation of a sulfinyl cation, which is generated in situ by dehydration of sulfinic acid. Then, intermediate **I** may be

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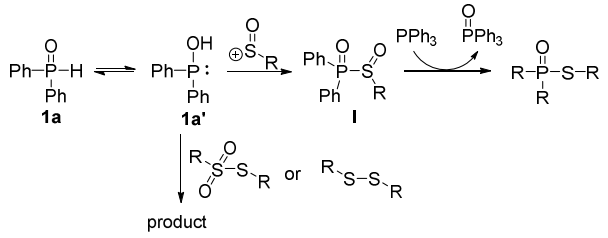
formed by nucleophilic attack of the P(III) form **1a'** on the sulfinyl cation. In the process, other mechanistic possibility involving reactive sulfur species such as such as sulfonothioate, sulfinothioate, or disulfide, can also be conceived.[14] Finally, intermediate **I** undergoes subsequent reduction by triphenylphosphine to afford the desired product **3**.



Scheme 5 Proposed reaction pathway.

Conclusions

In summary, we have developed an operationally simple method for S–P(O) bond formation metal-, oxidant-, and halogen-free conditions. The high reaction efficacy was realized by the addition of PPh_3 as a reductant. The current method is compatible with a broad range of substituents on various substrates including halogens and heterocyclic moieties, which are difficult to retain in transition metal- or peroxide-mediated reactions. The synthetic potential of this method was further highlighted by the expeditious synthesis of optically pure *P*-chiral phosphorothioates via simple stereospecific coupling reactions. Further studies on the application of this method to conjugation in chemical biology are currently underway.

Experimental

General information

Unless stated otherwise, reactions were performed in flame-dried glassware. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 F^{254} plates and visualization on TLC was achieved by UV light (254 and 365 nm). Flash column chromatography was undertaken on silica gel (400-630 mesh). ^{1}H NMR was recorded on 400 MHz and chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, td = doublet of triplet, ddd = doublet of doublet of doublet. Coupling constants, *J*, were reported in hertz unit (Hz). ^{13}C NMR was recorded on 100 MHz and was fully decoupled by broad band proton decoupling. Signals of ^{13}C spectra of carbon atom adjacent to phosphorus atom of organophosphorus compounds appeared as a doublet with varied coupling constants between C and P (J_{CP}). Chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of $CDCl_3$. ^{31}P NMR was recorded on 162 MHz and was fully decoupled by broad band proton decoupling. Mass spectral data were obtained from the KAIST Basic Science Institute by using ESI method. Commercial grade reagents and solvents were used without further purification except as indicated below.

General procedure

$R_1R_2P(O)H$ (1 equiv), sulfinic acid (2 equiv), and Ph_3P (1 equiv) were combined in *i*PrOAc (1.0 mL) under nitrogen condition in a seal tube. The reaction was stirred at room temperature for 24 h. The mixture was monitored by TLC using MeOH and CH_2Cl_2 = 1 : 20 as the mobile phase and stirred until starting material disappeared. The mixture solvent was removed under reduced pressure. The reaction mixture was diluted with CH_2Cl_2 and the residue was extracted with aqueous NH_4Cl (3 × 30 mL). The organic layer was dried over $MgSO_4$. After removal of solvent, the residue was purified by flash chromatography on silica gel to give desired product.

S-p-tolyl diphenylphosphinothioate (3a).[4c] From diphenylphosphine oxide (34.2 mg, 0.169 mol), compound **3a** (47.2 mg, 86%) was obtained. White solid. mp 116-118 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.74 (m, 4H), 7.54 – 7.36 (m, 6H), 7.30 (dd, *J* = 8.1, 1.8 Hz, 2H), 6.98 (d, *J* = 7.8 Hz, 2H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 139.1 (d, *J* = 2.4 Hz), 135.3 (d, *J* = 3.8 Hz), 132.7 (d, *J* = 106.7 Hz), 132.2 (d, *J* = 3.0 Hz), 131.6 (d, *J* = 10.3 Hz), 129.9 (d, *J* = 1.9 Hz), 128.5 (d, *J* = 13.1 Hz), 122.2 (d, *J* = 5.3 Hz), 21.1. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 42.0. HRMS (ESI^+) m/z calcd. $C_{19}H_{17}NaOPS^+$ $[M+Na]^+$: 347.0630, found: 347.0637.

S-o-tolyl diphenylphosphinothioate (3b).[5] From diphenylphosphine oxide (34.0 mg, 0.168 mol), compound **3b** (52.9 mg, 97%) was obtained. White solid. mp 72-74 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.74 (m, 4H), 7.52 – 7.32 (m, 7H), 7.16 – 7.05 (m, 2H), 6.97 (td, *J* = 7.4, 2.1 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.7 (d, *J* = 3.9 Hz), 136.6 (d, *J* = 3.7 Hz), 133.2, 132.1 (d, *J* = 3.2 Hz), 131.3 (d, *J* = 10.2 Hz), 130.5 (d, *J* = 2.2 Hz), 129.1 (d, *J* = 2.6 Hz), 128.3 (d, *J* = 13.0 Hz), 126.3 (d, *J* = 2.0 Hz), 125.3 (d, *J* = 5.3 Hz), 21.3. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 41.6. HRMS (ESI^+) m/z calcd. $C_{19}H_{17}NaOPS^+$ $[M+Na]^+$: 347.0630, found: 347.0625.

S-phenyl diphenylphosphinothioate (3c).[4c] From diphenylphosphine oxide (33.9 mg, 0.168 mol), compound **3c** (50.1 mg, 96%) was obtained. White solid. mp 92-94 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.76 (m, 4H), 7.54 – 7.34 (m, 8H), 7.22 – 7.11 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 135.2 (d, *J* = 3.9 Hz), 132.5 (d, *J* = 107.0 Hz), 132.2 (d, *J* = 3.0 Hz), 131.5 (d, *J* = 10.2 Hz), 129.0 (d, *J* = 1.8 Hz), 128.8 (d, *J* = 2.2 Hz), 128.4 (d, *J* = 13.2 Hz), 126.0 (d, *J* = 5.2 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 42.1. HRMS (ESI^+) m/z calcd. $C_{18}H_{15}NaOPS^+$ $[M+Na]^+$: 333.0473, found: 333.0479.

S-(4-(tert-butyl)phenyl) diphenylphosphinothioate (3d).[5] From diphenylphosphine oxide (34.0 mg, 0.168 mol), compound **3d** (59.8 mg, 97%) was obtained. White solid. mp 126-128 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (ddd, *J* = 12.9, 8.4, 1.4 Hz, 4H), 7.49 – 7.29 (m, 8H), 7.18 (d, *J* = 8.4 Hz, 2H), 1.19 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ

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152.1 (d, J = 2.5 Hz), 135.1 (d, J = 3.7 Hz), 132.7 (d, J = 106.7 Hz), 132.1 (d, J = 3.0 Hz), 131.5 (d, J = 10.3 Hz), 128.3 (d, J = 13.1 Hz), 126.1 (d, J = 1.9 Hz), 122.2 (d, J = 5.3 Hz), 34.4, 31.0. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 42.2. HRMS (ESI$^+$) m/z calcd. $C_{22}H_{23}NaOPS^+$ [M+Na]$^+$: 389.1099, found: 389.1097.

S-(4-fluorophenyl) diphenylphosphinothioate (3e).[5] From diphenylphosphine oxide (33.6 mg, 0.166 mol), compound **3e** (49.7 mg, 91%) was obtained. White solid. mp 111-113 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (ddd, J = 12.9, 8.4, 1.5 Hz, 4H), 7.53 – 7.31 (m, 8H), 6.86 (t, J = 8.6 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.3 (dd, J = 249.8, 2.5 Hz), 137.3 (dd, J = 8.6, 3.7 Hz), 132.4 (d, J = 3.1 Hz), 132.3 (d, J = 106.9 Hz), 131.5 (d, J = 10.3 Hz), 128.5 (d, J = 13.2 Hz), 121.1 (dd, J = 5.2, 3.4 Hz), 116.3 (dd, J = 21.9, 2.0 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 42.1 (d, J = 4.5 Hz). HRMS (ESI$^+$) m/z calcd. $C_{18}H_{14}FNaOPS^+$ [M+Na]$^+$: 351.0379, found: 351.0382.

S-(4-chlorophenyl) diphenylphosphinothioate (3f).[4c] From diphenylphosphine oxide (33.8 mg, 0.167 mol), compound **3f** (47.2 mg, 82%) was obtained. White solid. mp 114-116 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (ddd, J = 12.9, 8.4, 1.4 Hz, 4H), 7.54 – 7.47 (m, 2H), 7.43 (ddd, J = 8.5, 6.5, 3.7 Hz, 4H), 7.35 (dd, J = 8.5, 1.7 Hz, 2H), 7.15 (d, J = 8.5 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 136.5 (d, J = 3.9 Hz), 135.5 (d, J = 2.7 Hz), 132.5 (d, J = 3.0 Hz), 132.2 (d, J = 107.2 Hz), 131.6 (d, J = 10.3 Hz), 129.3 (d, J = 1.8 Hz), 128.6 (d, J = 13.2 Hz), 124.7 (d, J = 5.1 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 42.1. HRMS (ESI$^+$) m/z calcd. $C_{18}H_{14}ClNaOPS^+$ [M+Na]$^+$: 367.0084, found: 367.0091.

S-(4-bromophenyl) diphenylphosphinothioate (3g).[5] From diphenylphosphine oxide (33.5 mg, 0.166 mol), compound **3g** (48.2 mg, 75%) was obtained. White solid. mp 106-108 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (ddd, J = 13.0, 8.3, 1.4 Hz, 4H), 7.50 (td, J = 7.2, 1.6 Hz, 2H), 7.43 (ddd, J = 8.6, 6.7, 3.8 Hz, 4H), 7.29 (d, J = 1.3 Hz, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 136.7 (d, J = 3.9 Hz), 132.7, 132.5 (d, J = 3.0 Hz), 132.2 (d, J = 1.9 Hz), 131.5 (d, J = 10.3 Hz), 128.6 (d, J = 13.2 Hz), 125.3 (d, J = 5.2 Hz), 123.7 (d, J = 2.8 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 42.1. HRMS (ESI$^+$) m/z calcd. $C_{18}H_{14}BrNaOPS^+$ [M+Na]$^+$: 410.9579, found: 410.9567.

S-(4-iodophenyl) diphenylphosphinothioate (3h). From diphenylphosphine oxide (34.0 mg, 0.168 mol), compound **3h** (63.1 mg, 86%) was obtained. White solid. mp 102-104 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.73 (m, 4H), 7.52 – 7.35 (m, 8H), 7.14 (dd, J = 8.4, 1.7 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.1 (d, J = 1.7 Hz), 136.7 (d, J = 3.9 Hz), 132.6, 132.4 (d, J = 3.1 Hz), 131.5 (d, J = 10.2 Hz), 128.5 (d, J = 13.2 Hz), 126.2 (d, J = 5.2 Hz), 95.5 (d, J = 2.9 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 42.0. HRMS (ESI$^+$) m/z calcd. $C_{18}H_{14}INaOPS^+$ [M+Na]$^+$: 458.9440, found: 458.9449.

S-(4-(trifluoromethyl)phenyl) diphenylphosphinothioate (3i). From diphenylphosphine oxide (32.2 mg, 0.159 mol), compound **3i** (46.3 mg, 77%) was obtained. White solid. mp 98-100 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (ddd, J = 13.0, 8.3, 1.4 Hz, 4H), 7.57 (d, J = 8.1 Hz, 2H), 7.54 – 7.48 (m, 2H), 7.47 – 7.38 (m, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 135.2 (d, J = 4.0 Hz), 132.6 (d, J = 3.2 Hz), 132.6, 131.6 (d, J = 10.4 Hz), 130.8 (dd, J = 32.8, 2.1 Hz), 128.7 (d, J = 13.3 Hz), 125.8 (dt, J = 4.1, 2.0 Hz), 125.1, 122.4. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 42.3. HRMS (ESI$^+$) m/z calcd. $C_{19}H_{14}F_3NaOPS^+$ [M+Na]$^+$: 401.0347, found: 401.0346.

S-(4-(trifluoromethoxy)phenyl) diphenylphosphinothioate (3j). From diphenylphosphine oxide (34.3 mg, 0.170 mol), compound **3j** (54.2 mg, 81%) was obtained. White solid. mp 69-71 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.76 (m, 4H), 7.52 – 7.37 (m, 8H), 7.01 (dt, J = 7.9, 1.1 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 149.8 (t, J = 2.2 Hz), 136.8 (d, J = 3.7 Hz), 132.5 (d, J = 3.1 Hz), 132.0 (d, J = 107.1 Hz), 131.5 (d, J = 10.4 Hz), 128.6 (d, J = 13.2 Hz), 124.8 (d, J = 5.1 Hz), 121.3, 120.2 (q, J = 258.0 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 42.3. HRMS (ESI$^+$) m/z calcd. $C_{19}H_{14}F_3NaO_2PS^+$ [M+Na]$^+$: 417.0296, found: 417.0298.

S-(4-methoxyphenyl) diphenylphosphinothioate (3k).[4c] From diphenylphosphine oxide (31.7 mg, 0.157 mol), compound **3k** (50.1 mg, 94%) was obtained. White solid. mp 150-152 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (ddd, J = 12.8, 8.2, 1.4 Hz, 4H), 7.49 – 7.36 (m, 6H), 7.30 (dd, J = 8.8, 1.8 Hz, 2H), 6.72 – 6.66 (m, 2H), 3.68 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.3 (d, J = 2.2 Hz), 136.9 (d, J = 3.5 Hz), 132.5 (d, J = 106.2 Hz), 132.1 (d, J = 3.0 Hz), 131.5 (d, J = 10.1 Hz), 128.4 (d, J = 13.1 Hz), 115.9 (d, J = 5.2 Hz), 114.7 (d, J = 1.9 Hz), 55.1. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 41.9. HRMS (ESI$^+$) m/z calcd. $C_{19}H_{17}NaO_2PS^+$ [M+Na]$^+$: 363.0579, found: 363.0585.

S-(naphthalen-2-yl) diphenylphosphinothioate (3l).[5] From diphenylphosphine oxide (33.8 mg, 0.167 mol), compound **3l** (51.9 mg, 86%) was obtained. White solid. mp 128-130 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (t, J = 2.1 Hz, 1H), 7.86 (ddd, J = 12.9, 8.3, 1.4 Hz, 4H), 7.74 – 7.63 (m, 2H), 7.63 (d, J = 8.6 Hz, 1H), 7.51 – 7.34 (m, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 135.3 (d, J = 5.0 Hz), 133.4 (d, J = 1.8 Hz), 132.9 (d, J = 1.6 Hz), 132.5 (d, J = 106.8 Hz), 132.2 (d, J = 3.0 Hz), 131.5 (d, J = 10.3 Hz), 131.4 (d, J = 3.1 Hz), 128.6 (d, J = 1.4 Hz), 128.4 (d, J = 13.2 Hz), 127.7, 127.5, 126.8, 126.3, 123.4 (d, J = 5.5 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 42.1. HRMS (ESI$^+$) m/z calcd. $C_{22}H_{17}NaOPS^+$ [M+Na]$^+$: 383.0630, found: 383.0636.

S-isopropyl diphenylphosphinothioate (3m).[4c] From diphenylphosphine oxide (33.8 mg, 0.167 mol), compound **3m** (35.6 mg, 77%) was obtained. White solid. mp 106-108 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (ddd, J = 12.9, 8.2, 1.5 Hz, 4H), 7.52 – 7.40 (m, 6H), 3.40 (dhept, J = 9.8, 6.8 Hz, 1H), 1.32 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 133.9 (d, J = 107.0 Hz), 132.1 (d, J = 3.0 Hz), 131.4 (d, J = 10.3 Hz), 128.5 (d, J = 13.1 Hz), 36.9 (d, J = 2.5 Hz), 25.8 (d, J = 4.6 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 42.3. HRMS (ESI$^+$) m/z calcd. $C_{15}H_{17}NaOPS^+$ [M+Na]$^+$: 299.0630, found: 299.0629.

S-benzyl diphenylphosphinothioate (3n).[4c] From diphenylphosphine oxide (33.9 mg, 0.168 mol), compound **3n** (46.8 mg, 86%) was obtained. White solid. mp 87-89 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.81 (m, 4H), 7.53 –

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7.47 (m, 2H), 7.46 – 7.40 (m, 4H), 7.21 – 7.13 (m, 5H), 4.00 (d, J = 9.1 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 136.8 (d, J = 5.5 Hz), 133.0 (d, J = 106.9 Hz), 132.3 (d, J = 3.0 Hz), 131.5 (d, J = 10.5 Hz), 129.0, 128.7, 128.5 (d, J = 2.7 Hz), 127.4, 33.1 (d, J = 2.2 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 43.4. HRMS (ESI$^+$) m/z calcd. $C_{19}H_{17}NaOPS^+$ [M+Na]$^+$: 347.0630, found: 347.0633.

S-phenethyl diphenylphosphinothioate (3o). From diphenylphosphine oxide (33.9 mg, 0.168 mol), compound **3o** (48.2 mg, 85%) was obtained. Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.86 (m, 4H), 7.58 – 7.45 (m, 6H), 7.31 – 7.25 (m, 2H), 7.24 – 7.19 (m, 1H), 7.15 – 7.10 (m, 2H), 3.11 – 3.03 (m, 2H), 2.98 – 2.92 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 139.3, 133.2 (d, J = 107.1 Hz), 132.2 (d, J = 3.0 Hz), 131.4 (d, J = 10.4 Hz), 128.7, 128.5 (d, J = 1.5 Hz), 128.4, 126.5, 36.9 (d, J = 4.7 Hz), 30.3 (d, J = 2.2 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 43.8. HRMS (ESI$^+$) m/z calcd. $C_{20}H_{19}NaOPS^+$ [M+Na]$^+$: 361.0786, found: 361.0789.

S-cyclopropyl diphenylphosphinothioate (3p). From diphenylphosphine oxide (33.7 mg, 0.167 mol), compound **3p** (39.8 mg, 87%) was obtained. White solid. mp 78-80 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.82 (m, 4H), 7.54 – 7.41 (m, 6H), 1.92 (ttd, J = 7.6, 4.4, 2.1 Hz, 1H), 0.81 – 0.72 (m, 2H), 0.68 – 0.60 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 133.4 (d, J = 105.7 Hz), 132.2 (d, J = 3.0 Hz), 131.4 (d, J = 10.3 Hz), 128.5 (d, J = 12.9 Hz), 9.3 (d, J = 2.9 Hz), 7.6 (d, J = 5.3 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 43.1. HRMS (ESI$^+$) m/z calcd. $C_{15}H_{15}NaOPS^+$ [M+Na]$^+$: 297.0473, found: 297.0475.

S-(thiophen-2-yl) diphenylphosphinothioate (3q). From diphenylphosphine oxide (33.7 mg, 0.167 mol), compound **3q** (39.5 mg, 75%) was obtained. White solid. mp 86-88 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.80 (m, 4H), 7.56 – 7.50 (m, 2H), 7.45 (tdd, J = 8.3, 3.3, 1.3 Hz, 4H), 7.28 (ddd, J = 5.4, 2.1, 1.2 Hz, 1H), 7.11 (ddd, J = 3.8, 2.6, 1.3 Hz, 1H), 6.89 (dd, J = 5.4, 3.6 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 136.9 (d, J = 4.7 Hz), 132.5 (d, J = 3.1 Hz), 131.8 (d, J = 10.3 Hz), 131.7 (d, J = 105.9 Hz), 131.3 (d, J = 3.2 Hz), 128.6 (d, J = 13.2 Hz), 127.8 (d, J = 2.5 Hz), 122.0 (d, J = 5.8 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 42.3. HRMS (ESI$^+$) m/z calcd. $C_{16}H_{13}NaOPS_2^+$ [M+Na]$^+$: 339.0038, found: 339.0039.

S-(2,3-dihydrobenzofuran-5-yl) diphenylphosphinothioate (3r). From diphenylphosphine oxide (35.3 mg, 0.174 mol), compound **3r** (56.1 mg, 91%) was obtained. White solid. mp 137-139 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.77 (m, 4H), 7.53 – 7.45 (m, 2H), 7.45 – 7.38 (m, 4H), 7.27 (t, J = 1.6 Hz, 1H), 7.08 – 7.02 (m, 1H), 6.55 (d, J = 8.3 Hz, 1H), 4.49 (t, J = 8.7 Hz, 2H), 3.08 (t, J = 8.7 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.2 (d, J = 2.3 Hz), 135.8 (d, J = 3.8 Hz), 133.2, 132.6 (d, J = 3.2 Hz), 132.2 (d, J = 3.2 Hz), 131.6 (d, J = 10.2 Hz), 128.5 (d, J = 13.1 Hz), 128.4 (d, J = 1.8 Hz), 115.1 (d, J = 5.3 Hz), 110.0 (d, J = 2.0 Hz), 71.6, 29.4. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 41.9. HRMS (ESI$^+$) m/z calcd. $C_{20}H_{17}NaO_2PS^+$ [M+Na]$^+$: 375.0579, found: 375.0579.

O-ethyl S-(p-tolyl) phenylphosphonothioate (4a).[3b] From ethyl phenylphosphinate (23.0 mg, 0.136 mol), compound **3e** (29.7 mg, 75%.) was obtained. Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.59 (m, 2H), 7.50 – 7.43 (m, 1H), 7.38 – 7.30 (m, 2H), 7.13 (dd, J = 8.2, 2.0 Hz, 2H), 6.98 (d, J = 7.6 Hz, 2H), 4.40 – 4.22 (m, 2H), 2.26 (d, J = 1.9 Hz, 3H), 1.36 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 139.1 (d, J = 3.1 Hz), 135.3 (d, J = 4.1 Hz), 132.3 (d, J = 3.1 Hz), 131.4 (d, J = 10.5 Hz), 130.8, 129.9 (d, J = 2.4 Hz), 128.1 (d, J = 14.9 Hz), 122.8 (d, J = 5.8 Hz), 62.3 (d, J = 6.9 Hz), 21.1, 16.3 (d, J = 6.7 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 42.4. HRMS (ESI$^+$) m/z calcd. $C_{15}H_{17}NaO_2PS^+$ [M+Na]$^+$: 315.0579, found: 315.0581.

O,O-dimethyl S-p-tolyl phosphorothioate (4b).[3c] From dimethyl phosphonate (10.9 mg, 0.0986 mol), compound **4b** (11.9 mg, 52%) was obtained. From trimethyl phosphite (21.0 mg, 0.169 mol), compound **4b** (21.6 mg, 55%) was obtained. Colorless oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.42 (dd, J = 8.3, 2.1 Hz, 2H), 7.14 (d, J = 8.1 Hz, 2H), 3.79 (d, J = 12.6 Hz, 6H), 2.33 (d, J = 2.1 Hz, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 139.5 (d, J = 3.2 Hz), 134.6 (d, J = 5.1 Hz), 130.3 (d, J = 2.7 Hz), 122.3 (d, J = 7.5 Hz), 54.2 (d, J = 6.2 Hz), 21.2. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 26.6. HRMS (ESI$^+$) m/z calcd. $C_9H_{13}NaO_3PS^+$ [M+Na]$^+$: 255.0215, found: 255.0217.

O,O-diethyl S-(p-tolyl) phosphorothioate (4c).[3c] From dimethyl phosphonate (13.7 mg, 0.0994 mol), compound **4c** (16.8 mg, 65%) was obtained. From triethyl phosphite (28.8 mg, 0.173 mol), compound **4c** (27.5 mg, 61%) was obtained. Colorless oil. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.40 (dd, J = 8.2, 2.1 Hz, 2H), 7.12 (d, J = 7.8 Hz, 2H), 4.21 – 4.09 (m, 4H), 2.30 (d, J = 2.1 Hz, 3H), 1.27 (dd, J = 7.4, 6.5 Hz, 6H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 139.2 (d, J = 3.2 Hz), 134.5 (d, J = 4.9 Hz), 130.1 (d, J = 2.3 Hz), 122.7 (d, J = 7.3 Hz), 63.9 (d, J = 6.0 Hz), 21.1, 15.9 (d, J = 7.1 Hz). ^{31}P NMR (243 MHz, Chloroform-*d*) δ 23.3. HRMS (ESI$^+$) m/z calcd. $C_{11}H_{17}NaO_3PS^+$ [M+Na]$^+$: 283.0528, found: 283.0528.

O,O-diisopropyl S-p-tolyl phosphorothioate (4d).[3c] From diisopropyl phosphonate (17.1 mg, 0.103 mol), compound **4d** (19.8 mg, 67%) was obtained. From triisopropyl phosphite (36.0 mg, 0.173 mol), compound **4d** (33.4 mg, 67%) was obtained. Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (dd, J = 8.2, 2.1 Hz, 2H), 7.11 (dq, J = 7.9, 0.7 Hz, 2H), 4.73 (dhept, J = 8.7, 6.2 Hz, 2H), 2.31 (d, J = 1.7 Hz, 3H), 1.27 (dd, J = 26.0, 6.1 Hz, 12H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 138.9 (d, J = 2.9 Hz), 134.3 (d, J = 5.3 Hz), 130.0 (d, J = 2.2 Hz), 123.5 (d, J = 7.1 Hz), 73.2 (d, J = 6.8 Hz), 23.7 (dd, J = 50.6, 4.9 Hz), 21.2. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 20.8. HRMS (ESI$^+$) m/z calcd. $C_{13}H_{21}NaO_3PS^+$ [M+Na]$^+$: 311.0841, found: 311.0847.

O,O-dibutyl S-p-tolyl phosphorothioate (4e).[3c] From diphenylphosphine oxide (19.3 mg, 0.0996 mol), compound **4e** (19.2 mg, 61%) was obtained. Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (dd, J = 8.3, 2.1 Hz, 2H), 7.12 (dq, J = 7.9, 0.7 Hz, 2H), 4.16 – 4.01 (m, 4H), 2.32 (d, J = 2.1 Hz, 3H), 1.65 – 1.56 (m, 4H), 1.39 – 1.28 (m, 4H), 0.88 (t, J = 7.4 Hz, 6H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 139.2 (d, J = 3.0 Hz), 134.6 (d, J = 4.9 Hz), 130.1 (d, J = 2.4 Hz), 122.9 (d, J = 7.4 Hz), 67.7 (d, J = 6.5 Hz), 32.1 (d, J = 7.0 Hz), 21.2, 18.7, 13.6. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 24.0. HRMS (ESI$^+$)

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m/z calcd. $C_{15}H_{25}NaO_3PS^+$ $[M+Na]^+$: 339.1154, found: 339.1159.

O,O-diphenyl S-p-tolyl phosphorothioate (4f).[4a] From diphenyl phosphonate (24.5 mg, 0.105 mol), compound **4f** (22.7 mg, 61%) was obtained. From triphenyl phosphite (47.9 mg, 0.155 mol), compound **4f** (35.8 mg, 65%) was obtained. Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.29 (m, 6H), 7.22 – 7.16 (m, 6H), 7.15 – 7.10 (m, 2H), 2.34 (d, *J* = 2.3 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.4 (d, *J* = 8.3 Hz), 140.0 (d, *J* = 3.4 Hz), 135.3 (d, *J* = 5.3 Hz), 130.3 (d, *J* = 2.9 Hz), 129.7, 125.5 (d, *J* = 1.5 Hz), 121.2 (d, *J* = 7.8 Hz), 120.5 (d, *J* = 5.1 Hz), 21.2 (d, *J* = 1.3 Hz). ^{31}P NMR (243 MHz, Chloroform-*d*) δ 15.2. HRMS (ESI$^+$) m/z calcd. $C_{19}H_{17}NaO_3PS^+$ $[M+Na]^+$: 379.0528, found: 379.0524.

5,5-dimethyl-2-(p-tolylthio)-1,3,2-dioxaphosphinane 2-oxide (4g). From 5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide (15.4 mg, 0.103 mol), compound **4g** (16.8 mg, 60%) was obtained. White solid. mp 103-105 °C. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.49 (dd, *J* = 8.3, 2.1 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 4.18 (dd, *J* = 10.8, 3.7 Hz, 2H), 3.90 (ddt, *J* = 23.8, 11.3, 1.6 Hz, 2H), 2.32 (d, *J* = 2.0 Hz, 3H), 1.25 (s, 3H), 0.85 (s, 3H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 139.3 (d, *J* = 2.9 Hz), 134.5 (d, *J* = 5.1 Hz), 130.1 (d, *J* = 2.6 Hz), 120.8 (d, *J* = 6.5 Hz), 78.0 (d, *J* = 7.1 Hz), 32.3 (d, *J* = 6.9 Hz), 21.8, 21.0, 20.2. ^{31}P NMR (243 MHz, Chloroform-*d*) δ 15.2. HRMS (ESI$^+$) m/z calcd. $C_{12}H_{17}NaO_3PS^+$ $[M+Na]^+$: 295.0528, found: 295.0527.

6-(p-tolylthio)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (4h). From dibenzo[c,e][1,2]oxaphosphinine 6-oxide (36.8 mg, 0.170 mol), compound **4h** (51.9 mg, 90%) was obtained. Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (ddd, *J* = 14.6, 7.6, 1.4 Hz, 1H), 7.79 – 7.74 (m, 1H), 7.66 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.61 (ddt, *J* = 8.4, 7.5, 1.4 Hz, 1H), 7.43 (tdd, *J* = 7.5, 3.6, 1.0 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.16 – 7.09 (m, 2H), 7.05 (dd, *J* = 8.2, 2.2 Hz, 2H), 6.82 (d, *J* = 8.0 Hz, 2H), 2.17 (d, *J* = 2.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.4 (d, *J* = 9.6 Hz), 139.6 (d, *J* = 3.3 Hz), 136.2 (d, *J* = 7.3 Hz), 135.8 (d, *J* = 4.2 Hz), 133.6 (d, *J* = 2.6 Hz), 130.6 (d, *J* = 10.2 Hz), 130.3, 129.7 (d, *J* = 2.7 Hz), 128.3 (d, *J* = 14.9 Hz), 124.8 (d, *J* = 133.8 Hz), 124.8, 124.3, 123.1 (d, *J* = 11.4 Hz), 121.7 (d, *J* = 11.5 Hz), 120.3 (d, *J* = 6.3 Hz), 119.9 (d, *J* = 7.1 Hz), 21.0. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 35.0. HRMS (ESI$^+$) m/z calcd. $C_{19}H_{15}NaO_2PS^+$ $[M+Na]^+$: 361.0423, found: 361.0424.

S-(p-tolyl) di-tert-butylphosphinothioate (4i). From di-tert-butylphosphine oxide (27.7 mg, 0.171 mol), compound **4i** (40.7 mg, 84%) was obtained. White solid. mp 55-57 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 2.29 (s, 3H), 1.31 (d, *J* = 15.5 Hz, 18H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.1 (d, *J* = 1.6 Hz), 135.4 (d, *J* = 2.9 Hz), 129.6, 124.7 (d, *J* = 5.0 Hz), 41.1 (d, *J* = 54.8 Hz), 26.9, 21.1. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 81.0. HRMS (ESI$^+$) m/z calcd. $C_{15}H_{25}NaOPS^+$ $[M+Na]^+$: 307.1256, found: 307.1253.

S-(p-tolyl) isopropyl(phenyl)phosphinothioate (4j). From isopropyl(phenyl)phosphine oxide (27.8 mg, 0.163 mol), compound **4j** (39.8 mg, 83%) was obtained. Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.68 (m, 2H), 7.50 – 7.34 (m, 3H), 7.32 – 7.25 (m, 2H), 6.98 (d, *J* = 7.8 Hz, 2H), 2.35 – 2.18 (m, 4H), 1.18 (dddd, *J* = 60.4, 19.1, 7.1, 1.5 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.9 (d, *J* = 2.2 Hz), 135.3 (d, *J* = 3.5 Hz), 131.9 (d, *J* = 9.3 Hz), 131.9 (d, *J* = 2.9 Hz), 130.9 (d, *J* = 95.2 Hz), 129.8 (d, *J* = 1.7 Hz), 128.2 (d, *J* = 12.2 Hz), 121.9 (d, *J* = 5.2 Hz), 32.1 (d, *J* = 71.1 Hz), 21.1, 16.1 (dd, *J* = 74.2, 2.8 Hz). ^{31}P NMR (162 MHz, Chloroform-*d*) δ 59.3. HRMS (ESI$^+$) m/z calcd. $C_{16}H_{19}NaOPS^+$ $[M+Na]^+$: 313.0786, found: 313.0788.

S-(p-tolyl) di-p-tolylphosphinothioate (4k).[5] From di-p-tolylphosphine oxide (38.8 mg, 0.169 mol), compound **4k** (55.8 mg, 94%) was obtained. Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 – 7.66 (m, 4H), 7.31 (dd, *J* = 8.2, 1.7 Hz, 2H), 7.20 (dd, *J* = 8.1, 3.4 Hz, 4H), 6.97 (d, *J* = 7.9 Hz, 2H), 2.34 (s, 6H), 2.22 (d, *J* = 1.4 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.6 (d, *J* = 3.1 Hz), 138.8 (d, *J* = 2.3 Hz), 135.1 (d, *J* = 3.8 Hz), 131.5 (d, *J* = 10.6 Hz), 130.2, 129.8 (d, *J* = 1.8 Hz), 129.1 (d, *J* = 13.5 Hz), 122.7 (d, *J* = 5.2 Hz), 21.5 (d, *J* = 1.4 Hz), 21.1. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 42.3. HRMS (ESI$^+$) m/z calcd. $C_{21}H_{21}NaOPS^+$ $[M+Na]^+$: 375.0943, found: 375.0948.

S-(p-tolyl) bis(4-fluorophenyl)phosphinothioate (4l).[5] From bis(4-fluorophenyl)phosphine oxide (39.8 mg, 0.167 mol), compound **4l** (57.7 mg, 96%) was obtained. White solid. mp 102-104 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.76 (m, 4H), 7.27 (dd, *J* = 8.2, 1.8 Hz, 2H), 7.09 (ddd, *J* = 8.7, 6.7, 2.6 Hz, 4H), 6.99 (d, *J* = 7.9 Hz, 2H), 2.22 (d, *J* = 1.5 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.1 (dd, *J* = 254.4, 3.5 Hz), 139.4 (d, *J* = 2.5 Hz), 135.2 (d, *J* = 3.9 Hz), 134.1 (dd, *J* = 11.8, 8.9 Hz), 130.0 (d, *J* = 2.0 Hz), 128.4 (dd, *J* = 110.8, 3.3 Hz), 121.8 (d, *J* = 5.3 Hz), 115.9 (dd, *J* = 21.6, 14.4 Hz), 21.1. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 39.7. HRMS (ESI$^+$) m/z calcd. $C_{19}H_{15}F_2NaOPS^+$ $[M+Na]^+$: 383.0441, found: 383.0444.

S-(p-tolyl) bis(4-methoxyphenyl)phosphinothioate (4m). From bis(4-methoxyphenyl)phosphine oxide (28.7 mg, 0.109 mol), compound **4m** (31.5 mg, 75%) was obtained. White solid. mp 87-89 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.69 (m, 4H), 7.29 (dd, *J* = 8.2, 1.7 Hz, 2H), 6.97 (d, *J* = 7.9 Hz, 2H), 6.90 (dd, *J* = 8.9, 2.7 Hz, 4H), 3.79 (s, 6H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.6 (d, *J* = 3.1 Hz), 138.8 (d, *J* = 2.4 Hz), 135.1 (d, *J* = 3.8 Hz), 133.5 (d, *J* = 11.8 Hz), 129.8 (d, *J* = 1.8 Hz), 124.1 (d, *J* = 114.4 Hz), 123.0 (d, *J* = 5.2 Hz), 113.9 (d, *J* = 14.3 Hz), 55.3, 21.1. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 42.0. HRMS (ESI$^+$) m/z calcd. $C_{21}H_{21}NaO_3PS^+$ $[M+Na]^+$: 407.0841, found: 407.0841.

S-(p-tolyl) bis(4-(trifluoromethyl)phenyl)phosphinothioate (4n). From bis(4-(trifluoromethyl)phenyl)phosphine oxide (34.5 mg, 0.102 mol), compound **4n** (44.1 mg, 94%) was obtained. White solid. mp 139-141 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.92 (m, 4H), 7.70 (dd, *J* = 8.3, 2.9 Hz, 4H), 7.30 (dd, *J* = 8.2, 1.8 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 2.26 (d, *J* = 1.6 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 140.0 (d, *J* = 2.6 Hz), 136.4 (d, *J* = 104.6 Hz), 135.4 (d, *J* = 4.0 Hz), 134.3 (dd, *J* = 32.9, 3.1 Hz), 132.0 (d, *J* = 10.4 Hz), 130.3 (d, *J* = 2.1 Hz), 125.6 (dq, *J* = 13.3, 3.7 Hz), 123.4 (q, *J* = 272.9

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Hz), 120.6 (d, J = 5.4 Hz), 21.1. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 38.3. HRMS (ESI$^+$) m/z calcd. $C_{21}H_{15}F_6NaOPS^+$ [M+Na]$^+$: 483.0378, found: 483.0379.

S-(p-tolyl) bis(4-chlorophenyl)phosphinothioate (4o).[5] From bis(4-chlorophenyl)phosphine oxide (46.0 mg, 0.170 mol), compound **4o** (62.2 mg, 93%) was obtained. White solid. mp 125-127 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (dd, J = 12.3, 8.1 Hz, 4H), 7.43 – 7.34 (m, 4H), 7.28 (d, J = 7.8 Hz, 2H), 7.00 (d, J = 7.8 Hz, 2H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 139.5 (d, J = 2.5 Hz), 139.0 (d, J = 3.7 Hz), 135.2 (d, J = 3.8 Hz), 132.8 (d, J = 11.1 Hz), 130.8 (d, J = 108.9 Hz), 130.1 (d, J = 2.0 Hz), 128.9 (d, J = 13.8 Hz), 121.4 (d, J = 5.2 Hz), 21.1. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 39.6. HRMS (ESI$^+$) m/z calcd. $C_{19}H_{15}Cl_2NaOPS^+$ [M+Na]$^+$: 414.9850, found: 414.9854.

S-(p-tolyl) bis(4-(dimethylamino)phenyl)phosphinothioate (4p). From bis(4-(dimethylamino)phenyl)phosphine oxide (28.8 mg, 0.0999 mol), compound **4p** (33.6 mg, 82%) was obtained. White solid. mp 181-183 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.59 (m, 4H), 7.35 – 7.30 (m, 2H), 6.97 (d, J = 7.8 Hz, 2H), 6.68 – 6.60 (m, 4H), 2.97 (s, 12H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 152.4 (d, J = 2.7 Hz), 138.2, 134.9 (d, J = 3.8 Hz), 133.1 (d, J = 11.7 Hz), 129.7, 124.6 (d, J = 5.1 Hz), 118.2 (d, J = 119.3 Hz), 111.0 (d, J = 14.0 Hz), 40.0, 21.1. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 44.3. HRMS (ESI$^+$) m/z calcd. $C_{23}H_{27}N_2NaOPS^+$ [M+Na]$^+$: 433.1474, found: 433.1475.

S-(p-tolyl) bis(3,5-dimethylphenyl)phosphinothioate (4q). From bis(3,5-dimethylphenyl)phosphine oxide (43.9 mg, 0.170 mol), compound **4p** (56.3 mg, 87%) was obtained. White solid. mp 142-144 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.38 (m, 4H), 7.31 (dd, J = 8.2, 1.7 Hz, 2H), 7.12 – 7.05 (m, 2H), 6.99 (d, J = 7.9 Hz, 2H), 2.29 (s, 12H), 2.23 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.9 (d, J = 2.5 Hz), 138.1 (d, J = 13.8 Hz), 135.3 (d, J = 3.6 Hz), 133.8 (d, J = 3.1 Hz), 132.4 (d, J = 105.3 Hz), 129.8 (d, J = 1.9 Hz), 129.1 (d, J = 10.2 Hz), 122.7 (d, J = 5.2 Hz), 21.2, 21.1. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 43.1. HRMS (ESI$^+$) m/z calcd. $C_{23}H_{25}NaOPS^+$ [M+Na]$^+$: 403.1256, found: 403.1256.

S-(p-tolyl) di(naphthalen-2-yl)phosphinothioate (4r).[5] From di(naphthalen-2-yl)phosphine oxide (30.7 mg, 0.102 mol), compound **4p** (37.9 mg, 88%) was obtained. Yield 88%. mg. Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.47 (d, J = 14.8 Hz, 2H), 7.95 – 7.79 (m, 8H), 7.58 – 7.47 (m, 4H), 7.38 (dd, J = 8.1, 1.9 Hz, 2H), 6.94 (d, J = 7.8 Hz, 2H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 139.1 (d, J = 2.6 Hz), 135.2 (d, J = 3.8 Hz), 134.7 (d, J = 2.6 Hz), 133.9 (d, J = 9.5 Hz), 132.3 (d, J = 14.3 Hz), 129.9 (d, J = 2.0 Hz), 129.7 (d, J = 107.2 Hz), 128.9, 128.4 (d, J = 13.0 Hz), 128.3, 127.7, 126.9, 126.2 (d, J = 11.5 Hz), 122.1 (d, J = 5.2 Hz), 21.0. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 42.0. HRMS (ESI$^+$) m/z calcd. $C_{27}H_{21}NaOPS^+$ [M+Na]$^+$: 447.0943, found: 447.0941.

O-((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl) S-(p-tolyl) (S)-phenylphosphonothioate (5a).[3a] From 2-isopropyl-5-methylcyclohexyl phenylphosphinate (27.6 mg, 0.0985 mol), compound **5a** (31.7 mg, 80%) was obtained. Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 – 7.64 (m, 2H), 7.48 – 7.42 (m, 1H), 7.39 – 7.31 (m, 2H), 7.22 (dd, J = 8.2, 2.0 Hz, 2H), 7.00 – 6.96 (m, 2H), 4.48 (tdd, J = 10.7, 8.5, 4.5 Hz, 1H), 2.25 (d, J = 1.9 Hz, 3H), 2.23 – 2.08 (m, 2H), 1.69 – 1.59 (m, 2H), 1.41 (dddd, J = 14.7, 10.6, 6.0, 3.2 Hz, 2H), 1.14 (td, J = 12.2, 10.8 Hz, 1H), 1.08 – 0.96 (m, 1H), 0.92 (d, J = 7.0 Hz, 3H), 0.84 (dd, J = 13.2, 6.7 Hz, 7H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.9 (d, J = 2.9 Hz), 135.3 (d, J = 4.1 Hz), 133.3 (d, J = 149.2 Hz), 132.1 (d, J = 3.2 Hz), 131.4 (d, J = 10.6 Hz), 129.8 (d, J = 2.4 Hz), 128.0 (d, J = 14.9 Hz), 122.8 (d, J = 5.1 Hz), 79.6 (d, J = 8.4 Hz), 48.7 (d, J = 6.9 Hz), 43.4, 34.0, 31.6, 25.6, 22.9, 21.8, 21.1 (d, J = 3.3 Hz), 15.9. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 40.5. HRMS (ESI$^+$) m/z calcd. $C_{23}H_{31}NaO_2PS^+$ [M+Na]$^+$: 425.1675, found: 425.1671.

S-(4-(tert-butyl)phenyl) O-((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl) (S)-phenylphosphonothioate (5b).[3a] From 2-isopropyl-5-methylcyclohexyl phenylphosphinate (42.5 mg, 0.152 mol), compound **5b** (56.7 mg, 84%) was obtained. Yield 84%. mg. Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (ddd, J = 13.7, 8.3, 1.4 Hz, 2H), 7.49 – 7.43 (m, 1H), 7.35 (ddd, J = 8.5, 6.8, 4.5 Hz, 2H), 7.29 – 7.25 (m, 2H), 7.22 – 7.18 (m, 2H), 4.48 (tdd, J = 10.7, 8.4, 4.5 Hz, 1H), 2.24 – 2.08 (m, 2H), 1.71 – 1.58 (m, 2H), 1.46 – 1.35 (m, 2H), 1.24 (s, 9H), 1.14 (td, J = 12.2, 10.9 Hz, 1H), 1.02 (qd, J = 14.1, 13.6, 3.8 Hz, 1H), 0.91 (d, J = 7.0 Hz, 3H), 0.85 – 0.76 (m, 7H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 152.0 (d, J = 2.9 Hz), 135.0 (d, J = 4.3 Hz), 133.4 (d, J = 149.1 Hz), 132.1 (d, J = 3.2 Hz), 131.4 (d, J = 10.6 Hz), 128.0 (d, J = 14.8 Hz), 126.1 (d, J = 2.2 Hz), 123.0 (d, J = 5.2 Hz), 79.7 (d, J = 8.5 Hz), 48.7 (d, J = 6.9 Hz), 43.4, 34.6, 34.0, 31.6, 31.2, 25.6, 22.9, 21.9, 21.1, 15.9. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 40.5. HRMS (ESI$^+$) m/z calcd. $C_{26}H_{37}NaO_2PS^+$ [M+Na]$^+$: 467.2144, found: 467.2145.

(S)-O-((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl) S-(4-methoxyphenyl) phenylphosphonothioate (5c).[3a] From 2-isopropyl-5-methylcyclohexyl phenylphosphinate (33.8 mg, 0.120 mol), compound **5c** (39.4 mg, 78%) was obtained. Colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.61 (m, 2H), 7.49 – 7.42 (m, 1H), 7.39 – 7.31 (m, 2H), 7.27 – 7.20 (m, 2H), 6.75 – 6.67 (m, 2H), 4.48 (tdd, J = 10.7, 8.5, 4.5 Hz, 1H), 3.73 (s, 3H), 2.24 – 2.10 (m, 2H), 1.71 – 1.58 (m, 2H), 1.40 (dddd, J = 13.9, 6.0, 4.5, 2.7 Hz, 2H), 1.13 (td, J = 12.2, 10.9 Hz, 1H), 1.08 – 0.97 (m, 1H), 0.93 (d, J = 7.0 Hz, 3H), 0.89 – 0.79 (m, 7H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.3 (d, J = 2.7 Hz), 137.0 (d, J = 4.0 Hz), 133.3 (d, J = 148.6 Hz), 132.1 (d, J = 3.2 Hz), 131.4 (d, J = 10.6 Hz), 128.1 (d, J = 14.8 Hz), 116.7 (d, J = 5.2 Hz), 114.6 (d, J = 2.2 Hz), 79.6 (d, J = 8.4 Hz), 55.3, 48.7 (d, J = 6.8 Hz), 43.4, 34.0, 31.6, 25.6, 22.9, 21.9, 21.2, 16.0. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 40.5. HRMS (ESI$^+$) m/z calcd. $C_{23}H_{31}NaO_3PS^+$ [M+Na]$^+$: 441.1624, found: 441.1625.

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Metal- and Oxidant-Free S–P(O) Bond Construction via Direct Coupling of P(O)H with Sulfinic Acids

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A method for S–P(O) bond formation between $R_2P(O)H$ and sulfinic acids was developed under metal-, oxidant-, and halogen-free conditions.