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An Alternative Metal-Free Aerobic Oxidative Cross-Dehydrogenative Coupling of Sulfonyl Hydrazides with Secondary Phosphine Oxides

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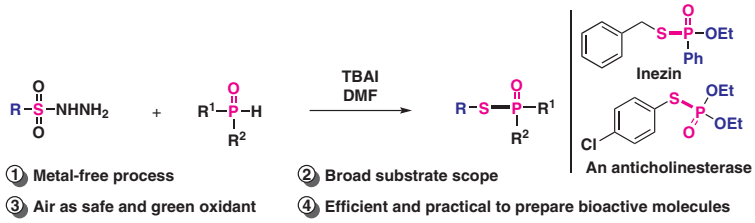

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Abstract An alternative metal-free, efficient and practical approach for the preparation of phosphinothioates is established via the aerobic oxidative cross-dehydrogenative coupling (CDC) of sulfonyl hydrazides with secondary phosphine oxides catalyzed by tetrabutylammonium iodide (TBAI) in the presence of atmospheric oxygen. The strategy provides an array of diverse phosphinothioates in good to excellent yields. Furthermore, two representative bioactive molecules are synthesized on up to gram scale by utilizing this method.

Key words phosphinothioates, metal-free, cross-dehydrogenative coupling, secondary phosphine oxides, sulfonyl hydrazides

Sulfur-containing organophosphorus derivatives have received considerable attention in recent decades, and many examples exhibit diverse biological activities as pesticides, insecticides, anticholinesterases, curing accelerators, antistatic agents and chemotherapeutic agents, etc. (Scheme 1, A).[1] Over the past decades, direct S–P cross-coupling reactions have proven to be among the most important and effective strategies to access phosphinothioate frameworks. In 1982, Michalski and co-workers reported the reaction of a sulfonic acid with a phosphamidazole at –60 °C to give, after oxidation, the corresponding phosphinothioate (Scheme 1, B, Route 1).[2] The groups of Kaboudin and Zhao have described multicomponent reactions (MCRs) for the preparation of phosphinothioates by utilizing diethyl phosphite, sulfur and alkyl halides or aryl boronic acids, respectively (Scheme 1, B, Route 2).[3] In addition, general methods for the preparation of phosphinothioates via nucleophilic substitution reactions of the moisture-sensitive and toxic halides [RSX, $R_2P(O)X$][4] and base-promoted Atherton–Todd type S–P(O) reactions[5] have been reported (Scheme 1, B, Routes 3 and 4).

For the past few years, transition-metal-catalyzed cross-coupling reactions of organosulfur compounds (diaryl disulfides and sulfonyl chlorides) with secondary phosphine oxides to construct S–P(O) bonds have been explored (Scheme 1, B, Route 5).[4e,5h,6] Very recently, the cross-dehydrogenative coupling (CDC) procedure has provided a straightforward and atom-economic approach to access phosphinothioates. However, many of the reported examples were highly dependent on the use of a stoichiometric strong oxidant, such as peroxides (TBPB, DTBP) and DDQ (Scheme 1, B, Route 6).[7]

Subsequently, Han et al. reported an oxidant-free, palladium-catalyzed dehydrogenative phosphorylation of RSH with $R_2P(O)H$ (Scheme 1, B, Route 6).[8] Thereafter, Zhang and co-workers developed two types of metal-free approaches via oxidative dehydrogenative processes for the preparation of phosphinothioates (Scheme 1, B, Route 6).[1y,9] In recent years, sulfonyl hydrazides, which are stable, non-corrosive, readily accessible and odorless sulfur sources, have been widely applied in organic synthesis.[10] In 2014, Kumaraswamy and Raju developed an aerobic dehydrogenative sulfenylation of secondary phosphine oxides with sulfonyl hydrazides catalyzed by CuI for the preparation of phosphinothioates (Scheme 1, B).[11] However, despite these advances, the involved starting materials, $R_2P(O)X$ (X = Cl, Br) and RSX (X = H, Cl, Br, CN, SAr), were often very odorous, toxic or moisture-sensitive reagents.[4–9] Furthermore, the aforementioned methods frequently required transition-metal catalysis and stoichiometric amounts of strong bases and oxidants.[4e,5h,6–8] Considering the importance of phosphinothioates in organic chemistry and biological chemistry, developing efficient, green and sustainable strategies to avoid the restrictions mentioned above are highly desirable, yet remain a formidable challenge.

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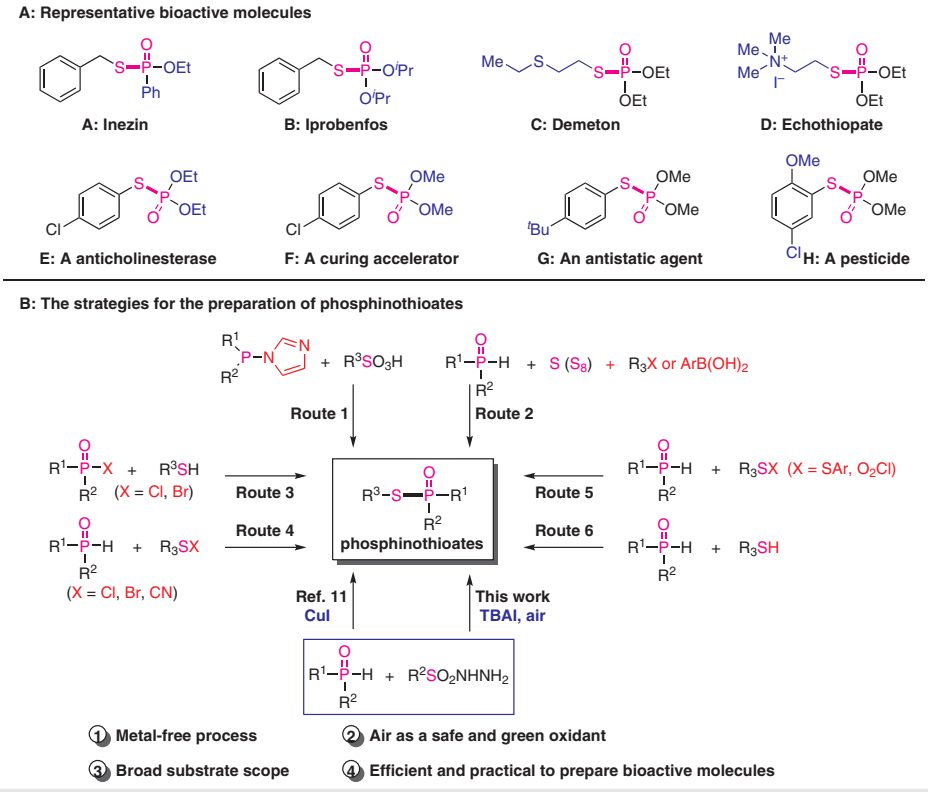


Scheme 1 Representative bioactive molecules and the strategies for the preparation of phosphinothioates

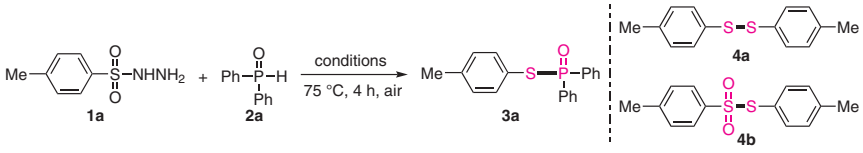
Atmospheric oxygen is a renewable, safe and green oxidant, which has been widely used in organic transformations. In continuation of our interest in constructing functional molecules via green synthetic strategies,[12] herein we describe a metal-free procedure for the cross-dehydrogenative coupling of secondary phosphine oxides with sulfonyl hydrazides catalyzed by tetrabutylammonium iodide (TBAI) in the presence of atmospheric oxygen (Scheme 1, B). Furthermore, our strategy can be applied to the preparation of representative bioactive molecules.

Our initial studies were directed toward investigation of the coupling of sulfonyl hydrazide **1a** and secondary phosphine oxide **2a**, as model substrates, at 75 °C in DMF under atmospheric oxygen (Table 1). In order to avoid metal iodide salts, TBAI was selected as the iodine source to catalyze this reaction. To our delight, the anticipated product **3a** was obtained in 81% yield, however, the dimerized compounds **4a** and **4b** were also isolated in 13% and 15% yield, respectively (Table 1, entry 1). The relative configuration of **3a** was determined by X-ray crystallographic analysis (Scheme 2).[13] In order to further improve the yield of the desired product **3a** and reduce the formation of dimerized compounds, other iodine sources were screened (NaI, KI, NIS), resulting in product **3a** being obtained in yields of 25–45% (Table 1, entries 2–4). Remarkably, no trace of the desired product **3a** was observed when using molecular iodine as the catalyst; instead, the dimerized compounds **4a** and **4b** were isolated in yields of 23% and 25%, respectively (Table 1, entry 5). Next, different solvents were screened, including toluene, CH_3CN, NMP, DMSO and 1,4-dioxane, and the results showed that DMF was the best reaction medium (Table 1, compare entries 1 and 6–10).

Furthermore, increasing or lowering the reaction temperature had adverse effects on the yield, with product **3a** being obtained in yields of 55% and 72% at temperatures of 65 °C and 85 °C, respectively (Table 1, entries 11 and 12). Ultimately, the optimum conditions for this coupling reaction required 20 mol% of TBAI as the catalyst, a temperature of 75 °C and DMF as the solvent, with **3a** being obtained in 81% yield.

Having optimized the conditions for the cross-dehydrogenative coupling process between secondary phosphine oxides and sulfonyl hydrazides, we next sought to explore the generality of this reaction. Firstly, aromatic sulfonyl hydrazides **1** with electron-rich [Me, OMe, ^{t}Bu, Ph, 2,4,6-$(Me)_3$] or electron-withdrawing (F, Cl, Br) substituents reacted with diphenylphosphine oxide (**2a**) to give the corresponding products in excellent yields (70–85%). Sterically hindered mesitylenesulfonyl hydrazide (**1f**) also reacted efficiently to give the desired product in a satisfactory 77%

Table 1 Optimization of the Reaction Conditions[a]

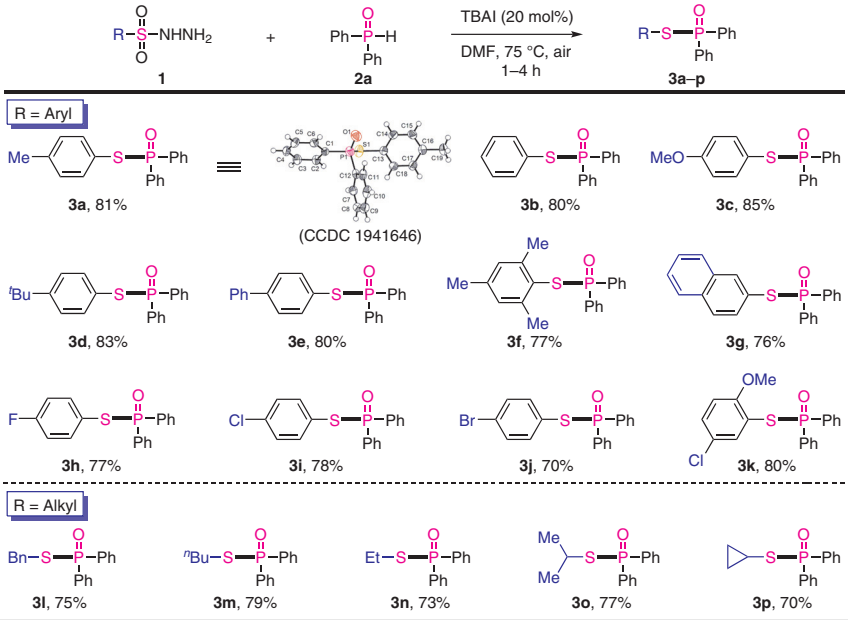


1a 2a 3a 4a 4b

Entry	Catalyst	Solvent	Yield (%)[b]
1	**TBAI**	**DMF**	**81**
2	NaI	DMF	45
3	KI	DMF	28
4	NIS	DMF	25
5	I_2	DMF	–
6	TBAI	toluene	61
7	TBAI	CH_3CN	50
8	TBAI	NMP	65
9	TBAI	DMSO	44
10	TBAI	1,4-dioxane	51
11[c]	TBAI	DMF	55
12[d]	TBAI	DMF	72

[a] Reaction conditions: **1a** (1.1 mmol), **2a** (1.0 mmol), catalyst (20 mol%), solvent (5.0 mL), air, 75 °C, 4 h.
[b] Yield of isolated product based on **2a**.
[c] Reaction temperature: 65 °C, reaction time: 5 h.
[d] Reaction temperature: 85 °C, reaction time: 2 h.

yield (Scheme 2). Furthermore, β-naphthylsulfonyl hydrazide (**1g**) was also compatible with this transformation, delivering the corresponding phosphinothioate **3g** in 76% yield. In addition, a sulfonyl hydrazide bearing an electron-donating methoxy substituent and an electron-withdrawing chlorine group on the aromatic nucleus provided the target product **3k** in 80% yield. More importantly, various aliphatic sulfonyl hydrazides containing straight-chain and



Scheme 2 Synthesis of phosphinothioates **3a–p**

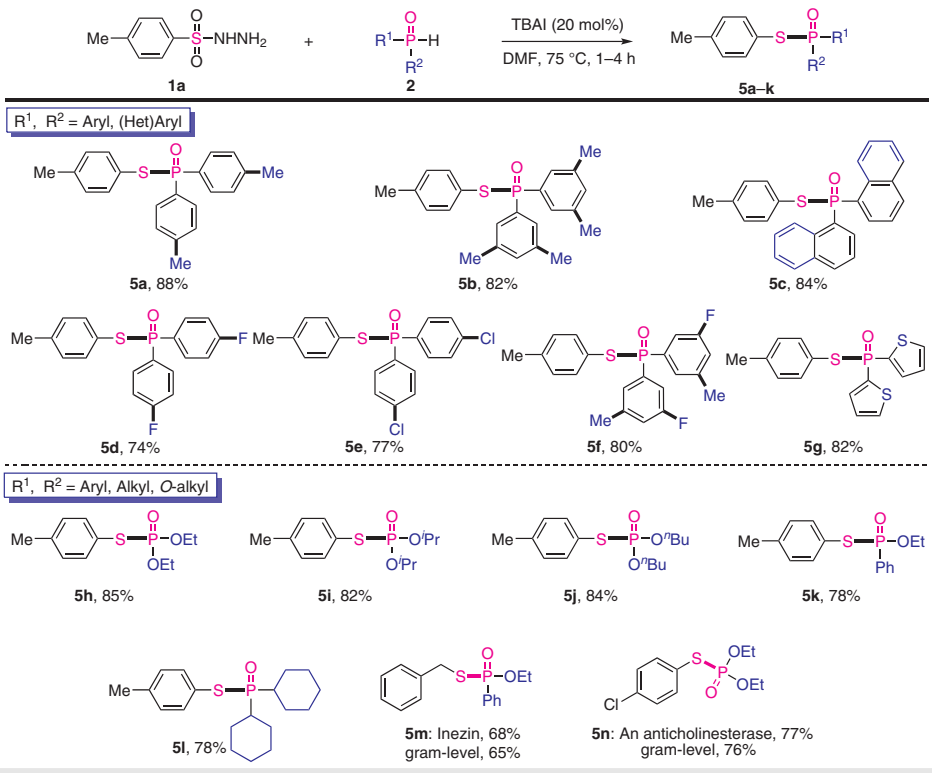
branched alkyl substituents also proved to be suitable substrates in this transformation, giving the corresponding phosphinothioates **3l–p** in yields of 70–79% (Scheme 2).

Under the optimized conditions, the substrate scope of various secondary phosphine oxides **2** was examined (Scheme 3). Diaryl-substituted phosphorus oxides with electron-donating substituents (R^1/R^2 = 4-Me-C_6H_4, α-naphthyl) or sterically hindered groups [R^1/R^2 = 3,5-$(Me)_2$-C_6H_3] reacted with 4-methylbenzenesulfonyl hydrazide (**1a**) to give the corresponding products **5a–c** in yields of 82–88%. In addition, diaryl-substituted phosphorus oxides with electron-withdrawing groups (4-F, 4-Cl), and even with both electron-donating (Me) and electron-withdrawing (F) groups, on the aromatic rings provided the corresponding products **5d–f** with 74–80% yields. Notably, a diheteroarylphosphine oxide was also well tolerated in this transformation, providing the desired product **5g** in a satisfactory 82% yield.

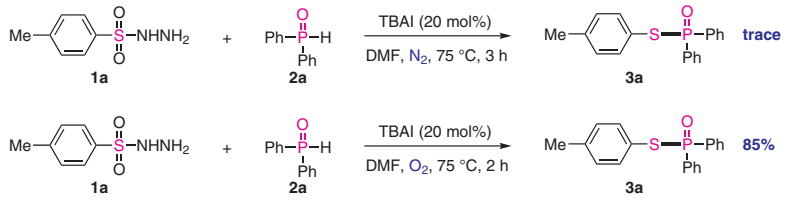
Subsequently, we turned our attention to phosphite diester substrates. To our delight, phosphite diesters such as diethyl phosphite, diisopropyl phosphite and dibutyl phosphite survived in this transformation, delivering the corresponding products **5h–k** in satisfactory yields of 78–85% (Scheme 3). Furthermore, a dialkyl-substituted phosphorus oxide was also compatible with this transformation, affording the desired product **5l** in 78% yield. To further demonstrate the potential utility of our strategy, two bioactive molecules, including the pesticide inezin (**5m**) and the anticholinesterase agent **5n**, were synthesized via this metal-free, aerobic cross-dehydrogenative coupling reaction. These reactions could also be scaled-up to gram level.

Additionally, to confirm that this reaction is an aerobic oxidative cross-dehydrogenative coupling process, several investigations were conducted. Indeed, under the standard conditions, the coupling reaction between **1a** and **2a** proceeded smoothly in the presence of an oxygen (O_2) atmosphere, but was sluggish when performed under a nitrogen (N_2) atmosphere (Scheme 4).

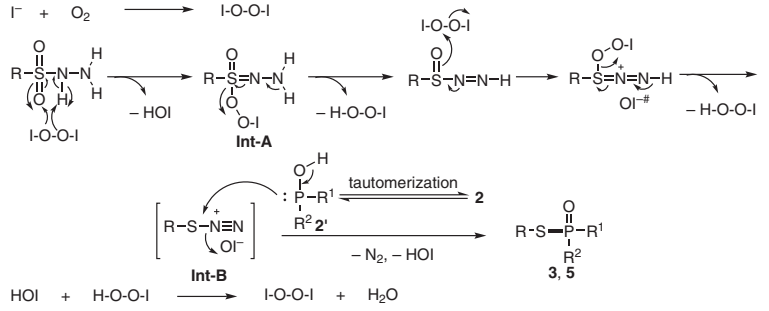
Based on the aforementioned results and previous reports, a plausible mechanism is proposed by analogy with cross-dehydrogenative coupling reactions.[11,14] Initially, iodine ions from TBAI react with oxygen to generate an iodine(I) peroxo species, which then dissociates in the presence of the sulfonyl hydrazide resulting in organic peroxide **Int-A** and hypoiodous acid (HOI). Next, sequential removal of hydrogen and oxygen atoms from putative **Int-A** could lead to thiodiazonium salt **Int-B**. Subsequently, the phosphorus atom of **2′** (i.e., the tautomer of **2**) attacks **Int-B** to form the desired phosphinothioates **3** or **5**, accompanied by release of nitrogen and hypoiodic acid (HOI). In these procedures, iodine ions are converted into the iodine(I) peroxo species, which then dissociates into HOI and HOOI, both of which react to give water and regenerate the iodine(I) peroxo species to continue the catalytic cycle (Scheme 5).



Scheme 3 Synthesis of phosphorus-containing thioates **5a–n**



Scheme 4 Confirmation of the aerobic oxidative cross-dehydrogenative coupling process



Scheme 5 Proposed reaction mechanism

In summary, an alternative metal-free, efficient and practical approach for the preparation of phosphinothioates has been established. The aerobic oxidative cross-dehydrogenative coupling (CDC) of sulfonyl hydrazides with secondary phosphine oxides catalyzed by TBAI in the presence of atmospheric oxygen provides an array of diverse phosphinothioates in good to excellent yields. Furthermore, several bioactive molecules could be prepared on up to gram scale via this method. Studies on the potential biological activity of the other compounds prepared in this work are currently under investigation in our laboratory.

All commercial reagents and solvents were used without further purification unless otherwise stated. Column chromatography was performed using Greagent silica gel (200–300 mesh). Melting points were determined on an XT-4A melting point apparatus and are uncorrected. NMR spectra were recorded on a Bruker 400 spectrometer (^{1}H, 400 MHz; ^{13}C, 100 MHz) with $CDCl_3$ as the solvent. The chemical shifts (δ) are expressed in parts per million relative to the residual deuterated solvent signal and coupling constants (*J*) are given in hertz. High-resolution mass spectrometry (ESI) was performed on an Agilent LC/MSD TOF instrument.

Sulfonyl Hydrazides 1; General Procedure[10]

To a stirred solution of the corresponding sulfonyl chloride (10 mmol, 1.0 equiv) in THF (20 mL) at 0 °C, hydrazine hydrate (11 mmol, 1.1 equiv) was added slowly. The reaction mixture was allowed to warm to ambient temperature and was stirred for over 1 h, with the progress monitored by TLC analysis. After the sulfonyl chloride had been completely consumed, the residue was extracted with EtOAc (2 × 20 mL). The combined organic layers were washed with H_2O (2 × 10 mL) and brine (2 × 5 mL) and then dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure to give the corresponding sulfonyl hydrazide **1**.

Secondary Phosphine Oxides 2; General Procedure[12c]

A mixture of magnesium turnings (3.3 mmol, 3.3 equiv), a small amount of iodine (ca. 3 pieces) and a small amount of 1-bromo-4-butylbenzene (ca. 5 drops) in THF (20 mL) was vigorously stirred under N_2. The flask was heated until the reaction was initiated (the solution became colorless). A solution of the corresponding aryl bromide (30.0 mmol, 3.0 equiv) in THF (30 mL) was added dropwise and the mixture stirred for 1 h. The flask was cooled to 0 °C using an ice bath and diethyl phosphite (1.30 mL, 10.0 mmol, 1.0 equiv) in THF (10 mL) was added over 30 min. After stirring for a further 2 h at room temperature, the reaction was quenched by the addition of 2 M HCl (20 mL) at 0 °C, and stirred for 15 min. The mixture was filtered through a Celite pad and the filtrate was extracted with EtOAc (×3). The combined organic layer was washed with brine and dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by flash column chromatography on silica gel (PE/EtOAc, 1:1) to afford the corresponding secondary phosphine oxide **2**.

Phosphorus-Containing Thioates 3 and 5; General Procedure[14]

A 10 mL round-bottomed flask was charged with sulfonyl hydrazide **1** (1.1 mmol, 1.1 equiv), secondary phosphine oxide **2** (1.0 mmol, 1.0 equiv) and TBAI (0.2 mmol, 0.2 equiv) in DMF (5 mL). The resulting solution was stirred for 1–4 h at 75 °C until the secondary phosphine oxide **2** had been completely consumed, as indicated by TLC. After, cooling, the reaction mixture was extracted with EtOAc (2 × 20 mL). The combined organic layers were washed with H_2O (2 × 10 mL) and brine (2 × 5 mL) and then dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the residue purified by flash column chromatography on silica gel (PE/EtOAc, 10:1 to 2:1) to afford the desired product **3** or **5**.

S-*p*-Tolyl Diphenylphosphinothioate (3a)

Yield: 262 mg (81%); yellow-white solid; mp 114–116 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82–7.87 (m, 4 H, ArH), 7.49–7.53 (m, 2 H, ArH), 7.42–7.46 (m, 4 H, ArH), 7.31–7.33 (m, 2 H, ArH), 7.01 (d, *J* = 8.0 Hz, 2 H, ArH), 2.25 (s, 3 H, $ArCH_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.2 (d, *J* = 3.7 Hz), 135.4 (d, *J* = 5.9 Hz), 133.2, 132.3, 132.2, 132.1, 130.0 (d, *J* = 3.0 Hz), 122.3 (d, *J* = 8.3 Hz), 122.2, 21.2.

^{31}P NMR (160 MHz, $CDCl_3$): δ = 41.3.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{17}OPSNa$: 347.0630; found: 347.0630.

S-Phenyl Diphenylphosphinothioate (3b)

Yield: 247 mg (80%); yellow-white solid; mp 108–110 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75–7.78 (m, 4 H, ArH), 7.42–7.47 (m, 2 H, ArH), 7.34–7.39 (m, 6 H, ArH), 7.10–7.20 (m, 3 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.4 (d, *J* = 6.1 Hz), 133.1, 132.3 (d, *J* = 4.6 Hz), 131.7 (d, *J* = 16.3 Hz), 129.1 (d, *J* = 2.2 Hz), 129.0 (d, *J* = 3.4 Hz), 128.6, 126.2, 126.1 (d, *J* = 8.2 Hz).

^{31}P NMR (160 MHz, $CDCl_3$): δ = 41.4.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{15}OPSNa$: 333.0473; found: 333.0472.

S-(4-Methoxyphenyl) Diphenylphosphinothioate (3c)

Yield: 289 mg (85%); yellow-white solid; mp 112–114 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81–7.83 (m, 4 H, ArH), 7.49–7.53 (m, 2 H, ArH), 7.42–7.47 (m, 4 H, ArH), 7.32–7.34 (m, 2 H, ArH), 6.73 (d, *J* = 8.4 Hz, 2 H, ArH), 3.74 (s, 3 H, $ArCH_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.5 (d, *J* = 3.2 Hz), 137.1 (d, *J* = 5.6 Hz), 133.2, 132.3, 132.2, 132.1, 131.7, 131.6, 128.6, 116.0 (d, *J* = 8.2 Hz), 114.8 (d, *J* = 2.6 Hz), 55.3.

^{31}P NMR (160 MHz, $CDCl_3$): δ = 41.3.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{17}O_2PSNa$: 363.0579; found: 363.0580.

S-[4-(*tert*-Butyl)phenyl] Diphenylphosphinothioate (3d)

Yield: 366 mg (83%); yellow-white solid; mp 112–114 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82–7.87 (m, 4 H, ArH), 7.50–7.54 (m, 2 H, ArH), 7.42–7.47 (m, 4 H, ArH), 7.34–7.36 (m, 2 H, ArH), 7.21–7.23 (m, 2 H, ArH), 1.24 (s, 9 H, $ArCH_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 152.3 (d, *J* = 3.8 Hz), 135.3 (d, *J* = 6.1 Hz), 135.2, 133.2, 132.3 (d, *J* = 4.8 Hz), 132.1, 131.7, 131.6, 128.6, 128.4, 126.3, 122.2 (d, *J* = 8.3 Hz), 34.6. 31.1.

^{31}P NMR (160 MHz, $CDCl_3$): δ = 41.7.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{23}OPSNa$: 389.1099; found: 389.1096.

S-([1,1′-Biphenyl]-4-yl) Diphenylphosphinothioate (3e)

Yield: 308 mg (80%); yellow-white solid; mp 100–102 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.91 (m, 4 H, ArH), 7.39–7.55 (m, 14 H, ArH), 7.31–7.36 (m, 1 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.8 (d, *J* = 3.5 Hz), 140.0 (d, *J* = 6.2 Hz), 135.8, 135.7, 133.1, 132.4, 132.3, 132.0, 131.7, 131.6, 128.8, 128.7, 128.5, 127.8, 127.7, 127.1, 125.0, 124.9 (d, *J* = 8.6 Hz).

^{31}P NMR (160 MHz, $CDCl_3$): δ = 41.5.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{24}H_{19}OPSNa$: 409.0786; found: 409.0785.

S-Mesityl Diphenylphosphinothioate (3f)

Yield: 271 mg (77%); yellow-white solid; mp 74–76 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74–7.79 (m, 4 H, ArH), 7.50–7.54 (m, 2 H, ArH), 7.40–7.45 (m, 4 H, ArH), 6.84 (s, 2 H, ArH), 2.24 (s, 6 H, $ArCH_3$), 2.23 (s, 3 H, $ArCH_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.8 (d, *J* = 5.1 Hz), 139.4 (d, *J* = 4.5 Hz), 139.3, 133.8, 132.8, 132.2, 131.4, 131.3, 129.4, 129.3, 128.5, 128.3, 120.8 (d, *J* = 9.6 Hz), 22.4, 21.1.

^{31}P NMR (160 MHz, $CDCl_3$): δ = 39.6.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{21}H_{21}OPSNa$: 375.0943; found: 375.0943.

S-(Naphthalen-2-yl) Diphenylphosphinothioate (3g)

Yield: 273 mg (76%); yellow-white solid; mp 142–144 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99 (s, 1 H, ArH), 7.85–7.90 (m, 4 H, ArH), 7.65–7.76 (m, 3 H, ArH), 7.41–7.53 (m, 9 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.4 (d, *J* = 8.0 Hz), 133.5, 133.1 (d, *J* = 11.8 Hz), 132.4 (d, *J* = 4.6 Hz), 132.0, 131.7, 131.6 (d, *J* = 5.3 Hz), 128.7, 128.6, 128.5, 127.8, 127.6, 126.9, 126.5, 123.5, 123.4 (d, *J* = 9.0 Hz).

^{31}P NMR (160 MHz, $CDCl_3$): δ = 41.5.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{17}OPSNa$: 383.0630; found: 383.0628.

S-(4-Fluorophenyl) Diphenylphosphinothioate (3h)

Yield: 252 mg (77%); yellow-white solid; mp 78–80 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81–7.86 (m, 4 H, ArH), 7.39–7.55 (m, 8 H, ArH), 6.88–6.92 (m, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.7, 162.2, 137.5 (d, *J* = 5.8), 137.4 (d, *J* = 5.8 Hz), 132.5, 132.4, 121.1, 116.5 (d, *J* = 2.2 Hz), 116.2 (d, *J* = 2.2 Hz), 116.3, 116.2.

^{31}P NMR (160 MHz, $CDCl_3$): δ = 41.7.

^{19}F NMR (160 MHz, $CDCl_3$): δ = –111.7.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{14}FOPSNa$: 351.0379; found: 351.0377.

S-(4-Chlorophenyl) Diphenylphosphinothioate (3i)

Yield: 268 mg (78%); yellow-white solid; mp 86–88 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81–7.87 (m, 4 H, ArH), 7.52–7.56 (m, 2 H, ArH), 7.44–7.49 (m, 4 H, ArH), 7.36–7.39 (m, 2 H, ArH), 7.16–7.20 (m, 2 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.6 (d, *J* = 6.2 Hz), 135.6 (d, *J* = 4.0 Hz), 135.5, 132.7, 132.6, 132.5, 129.4, 129.3, 124.7 (d, *J* = 8.3 Hz).

^{31}P NMR (160 MHz, $CDCl_3$): δ = 41.7.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{14}ClOPSNa$: 367.0084; found: 367.0080.

S-(4-Bromophenyl) Diphenylphosphinothioate (3j)

Yield: 271 mg (70%); yellow-white solid; mp 140–142 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81–8.05 (m, 4 H, ArH), 7.60–7.77 (m, 3 H, ArH), 7.52–7.55 (m, 2 H, ArH), 7.42–7.48 (m, 4 H, ArH), 7.35–7.39 (m, 1 H, ArH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.8 (d, *J* = 5.9 Hz), 132.7, 132.5, 132.3, 132.2, 131.6, 131.3, 131.2, 129.4, 128.7, 128.6, 128.2, 128.0, 125.4 (d, *J* = 9.6 Hz), 123.8 (d, *J* = 7.7 Hz).

^{31}P NMR (160 MHz, $CDCl_3$): δ = 41.4.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{18}H_{14}BrOPSNa$: 410.9579; found: 410.9578.

S-(5-Chloro-2-methoxyphenyl) Diphenylphosphinothioate (3k)

Yield: 299 mg (80%); yellow-white solid; mp 112–114 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.90 (m, 4 H, ArH), 7.61–7.62 (m, 1 H, ArH), 7.50–7.54 (m, 2 H, ArH), 7.42–7.47 (m, 4 H, ArH), 7.17–7.20 (m, 1 H, ArH), 6.64 (d, *J* = 8.8 Hz, 1 H, ArH), 3.61 (s, 3 H, $ArOCH_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.3 (d, *J* = 5.6 Hz), 136.8 (d, *J* = 6.4 Hz), 133.2, 132.4, 132.3, 132.2, 130.5, 125.6 (d, *J* = 3.0 Hz), 115.9 (d, *J* = 8.2 Hz), 112.0 (d, *J* = 2.7 Hz), 55.9.

^{31}P NMR (160 MHz, $CDCl_3$): δ = 41.6.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{16}ClO_2PSNa$: 397.0189; found: 397.0189.

S-Benzyl Diphenylphosphinothioate (3l)

Yield: 243 mg (75%); yellow-white oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.89 (m, 4 H, ArH), 7.52–7.56 (m, 2 H, ArH), 7.36–7.49 (m, 4 H, ArH), 7.18–7.22 (m, 5 H, ArH), 4.03 (d, *J* = 8.8 Hz, 2 H, $ArCH_2$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.8, 133.5, 132.4, 132.3, 131.6, 131.5, 129.1, 128.8, 128.6 (d, *J* = 5.4 Hz), 127.5, 33.2.

^{31}P NMR (160 MHz, $CDCl_3$): δ = 42.9.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{17}OPSNa$: 347.0630; found: 347.0631.

S-Butyl Diphenylphosphinothioate (3m)

Yield: 229 mg (79%); yellow-white oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.91 (m, 4 H, ArH), 7.46–7.56 (m, 6 H, ArH), 2.77–2.83 (m, 2 H, CH_2), 1.57–1.64 (m, 2 H, CH_2), 1.31–1.43 (m, 2 H, CH_2), 0.84 (t, *J* = 7.2 Hz, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.9, 132.9, 132.3, 132.2, 131.5,131.4, 128.7, 128.6, 32.6 (d, *J* = 8.0Hz), 32.5, 29.7, 29.0 (d, *J* = 3.4 Hz), 21.8, 13.5.

^{31}P NMR (160 MHz, $CDCl_3$): δ = 43.3.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{19}OPSNa$: 313.0786; found: 313.0785.

S-Ethyl Diphenylphosphinothioate (3n)

Yield: 191 mg (73%); yellow-white oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.91 (m, 4 H, ArH), 7.46–7.57 (m, 6 H, ArH), 2.79–2.87 (m, 2 H, CH_2), 1.30 (t, *J* = 7.2 Hz, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.8, 132.8, 132.3, 132.2, 131.6, 131.5, 129.5, 128.8, 128.6, 115.4, 23.9 (d, *J* = 4.2 Hz), 16.3 (d, *J* = 8.5 Hz).

^{31}P NMR (160 MHz, $CDCl_3$): δ = 43.4.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{15}OPSNa$: 285.0473; found: 285.0474.

S-Isopropyl Diphenylphosphinothioate (3o)

Yield: 212 mg (77%); yellow-white oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.91 (m, 4 H, ArH), 7.46–7.55 (m, 6 H, ArH), 3.38–3.47 (m, 1 H, CH), 1.36 (s, 3 H, CH_3), 1.35 (s, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.3, 133.2, 132.2, 132.1, 131.6, 131.4, 128.7, 128.6, 37.0 (d, *J* = 3.8 Hz), 25.8 (d, *J* = 7.2 Hz).

^{31}P NMR (160 MHz, $CDCl_3$): δ = 41.9.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{17}OPSNa$: 299.0630; found: 299.0631.

S-Cyclopropyl Diphenylphosphinothioate (3p)

Yield: 191 mg (70%); yellow-white oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.92 (m, 4 H, ArH), 7.55–7.58 (m, 6 H, ArH), 1.92–1.99 (m, 1 H, CH), 0.78–0.83 (m, 2 H, CH_2), 0.67–0.69 (m, 2 H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.8, 132.7, 132.3 (d, *J* = 4.8 Hz), 131.6, 131.5, 129.5, 128.7, 128.6, 128.1, 126.4, 115.4, 31.1, 9.39 (d, *J* = 4.5 Hz), 7.73 (d, *J* = 8.6 Hz).

^{31}P NMR (160 MHz, $CDCl_3$): δ = 42.9.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{15}OPSNa$: 297.0473; found: 297.0475.

S-(*p*-Tolyl) Di-*p*-tolylphosphinothioate (5a)

Yield: 310 mg (88%); yellow-white solid; mp 102–104 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.69–7.75 (m, 4 H, ArH), 7.32–7.33 (m, 2 H, ArH), 7.22–7.26 (m, 4 H, ArH), 7.01 (d, *J* = 8.0 Hz, 2 H, ArH), 2.38 (s, 6 H, $ArCH_3$), 2.26 (s, 3 H, $ArCH_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.8 (d, *J* = 4.6 Hz), 139.0 (d, *J* = 3.5 Hz), 138.9, 135.3 (d, *J* = 5.6 Hz), 131.7, 131.6, 130.2, 130.0, 129.9, 129.3, 129.2, 129.1, 122.8, 122.7, 21.7, 21.2.

^{31}P NMR (160 MHz, $CDCl_3$): δ = 41.9.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{21}H_{21}OPSNa$: 375.0943; found: 375.0945.

S-(*p*-Tolyl) Bis(3,5-dimethylphenyl)phosphinothioate (5b)

Yield: 311 mg (82%); yellow-white solid; mp 118–120 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.46 (m, 4 H, ArH), 7.32–7.33 (m, 2 H, ArH), 7.12 (s, 2 H, ArH), 7.02 (d, *J* = 7.6 Hz, 2 H, ArH), 2.32 (s, 12 H, $ArCH_3$), 2.27 (s, 3 H, $ArCH_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.0 (d, *J* = 3.8 Hz), 138.3, 138.1, 135.4 (d, *J* = 5.9 Hz), 134.0 (d, *J* = 4.8 Hz), 133.0, 131.9, 129.9 (d, *J* = 2.1 Hz), 122.7 (d, *J* = 8.5 Hz), 21.3, 21.2.

^{31}P NMR (160 MHz, $CDCl_3$): δ = 42.6.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{23}H_{25}OPSNa$: 403.1256; found: 403.1253.

S-(*p*-Tolyl) Di(naphthalen-1-yl)phosphinothioate (5c)

Yield: 356 mg (84%); yellow-white solid; mp 128–130 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.84–8.87 (m, 2 H, ArH), 8.06–8.08 (m, 1 H, ArH), 8.00–8.03 (s, 3 H, ArH), 7.88–7.90 (m, 2 H, ArH), 7.51–7.54 (m, 4 H, ArH), 7.42–7.50 (m, 2 H, ArH), 7.34–7.37 (m, 2 H, ArH), 6.97 (d, *J* = 8.0 Hz, 2 H, ArH), 2.23 (s, 3 H, $ArCH_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.1 (d, *J* = 3.8 Hz), 135.4 (d, *J* = 6.1 Hz), 134.0, 133.9, 133.7 (d, *J* = 5.3 Hz), 133.5, 133.3, 133.2, 129.9 (d, *J* = 2.9 Hz),129.6 (d, *J* = 4.3 Hz), 128.8, 128.5, 127.3 (d, *J* = 7.8 Hz), 126.5, 126.0, 124.5, 124.3, 123.0 (d, *J* = 8.5 Hz), 21.2.

^{31}P NMR (160 MHz, $CDCl_3$): δ = 45.3.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{27}H_{21}OPSNa$: 447.0943; found: 447.0940.

S-(*p*-Tolyl) Bis(4-fluorophenyl)phosphinothioate (5d)

Yield: 266 mg (74%); yellow-white solid; mp 123–125 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.87 (m, 4 H, ArH), 7.29–7.31 (m, 2 H, ArH), 7.12–7.17 (s, 4 H, ArH), 7.03–7.05 (m, 2 H, ArH), 2.28 (s, 3 H, $ArCH_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.6, 164.0, 139.5, 135.3 (d, *J* = 6.1 Hz), 134.3 (d, *J* = 3.5 Hz), 134.2 (d, *J* = 14.1 Hz), 130.2 (d, *J* = 2.7 Hz), 127.8, 121.7, 116.2, 116.1, 116.0, 115.9, 21.2.

^{31}P NMR (160 MHz, $CDCl_3$): δ = 39.3.

^{19}F NMR (160 MHz, $CDCl_3$): δ = –105.7.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{15}F_2OPSNa$: 383.0441; found: 383.0440.

S-(*p*-Tolyl) Bis(4-chlorophenyl)phosphinothioate (5e)

Yield: 301 mg (77%); yellow-white solid; mp 102–104 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73–7.78 (m, 4 H, ArH), 7.42–7.44 (m, 4 H, ArH), 7.29–7.32 (m, 2 H, ArH), 7.04 (d, *J* = 8.0 Hz, 2 H, ArH), 2.28 (s, 3 H, $ArCH_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.7 (d, *J* = 3.5 Hz), 139.2 (d, *J* = 5.8 Hz), 135.4 (d, *J* = 6.2 Hz), 133.0, 132.9, 131.4, 130.3 (d, *J* = 13.1 Hz), 130.2, 129.1, 129.0, 121.5, 121.4 (d, *J* = 7.0 Hz), 21.2.

^{31}P NMR (160 MHz, $CDCl_3$): δ = 39.2.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{15}Cl_2OPSNa$: 414.9850; found: 414.9851.

S-(*p*-Tolyl) Bis(3-fluoro-5-methylphenyl)phosphinothioate (5f)

Yield: 310 mg (80%); yellow-white solid; mp 108–110 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.46 (m, 2 H, ArH), 7.28–7.35 (m, 4 H, ArH), 7.02–7.06 (m, 4 H, ArH), 2.37 (s, 6 H, $ArCH_3$), 2.28 (s, 3 H, $ArCH_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.7 (d, $J_{c\text{-}F}$= 32.0 Hz), 161.2 (d, $J_{c\text{-}F}$= 31.7 Hz), 141.6 (d, *J* = 11.5 Hz), 141.5 (d, *J* = 11.7 Hz), 139.7 (d, *J* = 4.2 Hz), 135.5, 135.4, 134.8 (d, *J* = 10.1 Hz), 133.7 (d, *J* = 10.1 Hz), 130.2, 130.1, 128.1 (d, *J* = 4.5 Hz), 127.9 (d, *J* = 4.0 Hz), 121.4 (d, *J* = 8.8 Hz), 120.4 (d, *J* = 4.3 Hz), 120.2 (d, *J* = 4.3 Hz), 115.5, 115.4, 115.3, 115.1, 21.3 (d, *J* = 20.8 Hz).

^{31}P NMR (160 MHz, $CDCl_3$): δ = 39.2.

^{19}F NMR (160 MHz, $CDCl_3$): δ = –112.0.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{21}H_{19}F_2OPSNa$: 411.0754; found: 411.0750.

S-(*p*-Tolyl) Di(thiophen-2-yl)phosphinothioate (5g)

Yield: 274 mg (82%); yellow-white solid; mp 99–101 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.72–7.75 (m, 2 H, ArH), 7.64–7.67 (m, 2 H, ArH), 7.38–7.40 (m, 2 H, ArH), 7.15–7.17 (m, 2 H, ArH), 7.07 (d, *J* = 8.0 Hz, 2 H, ArH), 2.29 (s, 3 H, $ArCH_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.5, 136.9 (d, *J* = 17.4 Hz), 136.8, 135.3 (d, *J* = 6.9 Hz), 134.6, 134.5 (d, *J* = 9.3 Hz), 133.4, 130.1 (d, *J* = 3.4 Hz), 128.4, 128.2, 122.3 (d, *J* = 8.8 Hz), 21.2.

^{31}P NMR (160 MHz, $CDCl_3$): δ = 23.1.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{13}OPS_3Na$: 358.9758; found: 358.9756.

O,O-Diethyl S-(*p*-Tolyl) Phosphorothioate (5h)

Yield: 221 mg (85%); yellow-white oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.45 (m, 2 H, ArH), 7.15–7.17 (m, 2 H, ArH), 4.16–4.27 (m, 4 H, CH_2), 2.35 (s, 3 H, $ArCH_3$), 1.31 (t, *J* = 7.2 Hz, 6 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.4, 134.7 (d, *J* = 7.7 Hz), 130.2 (d, *J* = 3.5 Hz), 122.8 (d, *J* = 11.4 Hz), 64.0 (d, *J* = 9.0Hz), 21.2, 16.1 (d, *J* = 11.7 Hz).

^{31}P NMR (160 MHz, $CDCl_3$): δ = 23.4.

HRMS (ESI-TOF): *m*/*z* calcd for $C_{11}H_{17}O_3PSNa$: 283.0528; found: 283.0525.

O,O-Diisopropyl S-(*p*-Tolyl) Phosphorothioate (5i)

Yield: 236 mg (82%); yellow-white oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.48 (m, 2 H, ArH), 7.14–7.16 (m, 2 H, ArH), 4.72–4.80 (m, 2 H, CH), 2.34 (s, 3 H, $ArCH_3$), 1.33 (d, *J* = 6.0 Hz, 6 H, CH_3), 1.27 (d, *J* = 6.4 Hz, 6 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.0 (d, *J* = 4.6 Hz), 134.4 (d, *J* = 8.3 Hz), 130.1 (d, *J* = 3.5 Hz), 123.5 (d, *J* = 11.0 Hz), 73.3 (d, *J* = 10.7 Hz), 23.9 (d, *J* = 6.7 Hz), 23.6 (d, *J* = 9.1 Hz), 21.2.

^{31}P NMR (160 MHz, $CDCl_3$): δ = 21.0.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{21}O_3PSNa$: 311.0841; found: 311.0840.

O,O-Dibutyl S-(*p*-Tolyl) Phosphorothioate (5j)

Yield: 265 mg (84%); yellow-white oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.45 (m, 2 H, ArH), 7.14–7.16 (m, 2 H, ArH), 4.04–4.18 (m, 4 H, CH_2), 2.34 (s, 3 H, $ArCH_3$), 1.61–1.66 (m, 4 H, CH_2), 1.31–1.40 (m, 4 H, CH_2), 0.90 (t, *J* = 7.2 Hz, 6 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.3 (d, *J* = 4.8 Hz), 134.6 (d, *J* = 8.2 Hz), 130.2 (d, *J* = 3.8 Hz), 122.9 (d, *J* = 11.5 Hz), 67.8 (d, *J* = 10.4 Hz), 32.2 (d, *J* = 11.5 Hz), 21.2, 18.7, 13.6.

^{31}P NMR (160 MHz, $CDCl_3$): δ = 23.5.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{25}O_3PSNa$: 339.1154; found: 339.1150.

(*S*)-O-Ethyl S-(*p*-Tolyl) Phenylphosphonothioate (5k)

Yield: 227 mg (78%); yellow-white oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.63–7.69 (m, 2 H, ArH), 7.49–7.52 (m, 1 H, ArH), 7.36–7.41 (m, 2 H, ArH), 7.15–7.17 (m, 2 H, ArH), 7.01–7.03 (m, 2 H, ArH), 4.27–4.42 (m, 2 H, ArH), 2.30 (s, 3 H, $ArCH_3$), 1.40 (t, *J* = 7.2 Hz, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.3 (d, *J* = 4.5 Hz), 135.5 (d, *J* = 6.7 Hz), 132.5 (d, *J* = 5.1 Hz), 131.6 (d, *J* = 17.0 Hz), 130.0 (d, *J* = 3.5 Hz), 128.3, 128.1, 62.4 (d, *J* = 10.9 Hz), 21.2, 16.4 (d, *J* = 10.9 Hz).

^{31}P NMR (160 MHz, $CDCl_3$): δ = 41.9.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{17}O_2PSNa$: 315.0579; found: 315.0577.

S-(*p*-Tolyl) Dicyclohexylphosphinothioate (5l)

Yield: 262 mg (78%); yellow-white oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 7.2 Hz, 2 H, ArH), 7.13 (d, *J* = 8.0 Hz, 2 H, ArH), 2.33 (s, 3 H, $ArCH_3$), 1.92–2.03 (m, 6 H, CH, CH_2), 1.82–1.83 (m, 4 H, CH_2), 1.69–1.74 (m, 3 H, CH_2), 1.38–1.52 (m, 4 H, CH_2), 1.20–1.22 (m, 5 H, CH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.7, 135.5 (d, *J* = 4.8 Hz), 130.0, 123.0 (d, *J* = 8.0 Hz), 40.4, 39.7, 26.6, 26.5, 26.4, 26.3, 26.2, 26.0, 25.9, 25.8, 21.2.

^{31}P NMR (160 MHz, $CDCl_3$): δ = 67.4.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{29}OPSNa$: 359.1569; found: 359.1570.

(*S*)-*S*-Benzyl *O*-Ethyl Phenylphosphonothioate (5m)

Yield: 198 mg (68%); yellow-white oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79–7.82 (m, 2 H, ArH), 7.52–7.57 (m, 1 H, ArH), 7.43–7.48 (m, 3 H, ArH), 7.20–7.25 (m, 4 H, ArH), 4.08–4.29 (m, 2H, CH2), 3.87–4.02 (m, 2H, CH2), 1.34 (t, *J* = 7.2 Hz, 3 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.2, 137.2 (d, *J* = 8.5 Hz), 132.6 (d, *J* = 5.0 Hz), 131.7 (d, *J* = 17.6 Hz), 131.3 (d, *J* = 17.6 Hz), 130.9 (d, *J* = 14.9 Hz), 129.0 (d, *J* = 11.0 Hz), 128.5 (d, *J* = 19.8 Hz), 127.5 (d, *J* = 4.6 Hz), 34.5 (d, *J* = 4.2 Hz), 16.3 (d, *J* = 11.2 Hz).

^{31}P NMR (160 MHz, $CDCl_3$): δ = 43.7.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{17}O_2PSNa$: 315.0579; found: 315.0575.

***S*-(4-Chlorophenyl) *O*,*O*-Diethyl Phosphorothioate (5n)**

Yield: 215 mg (77%); yellow-white oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.52 (m, 2 H, ArH), 7.32–7.34 (m, 2 H, ArH), 4.12–4.27 (m, 4 H, CH_2), 1.30–1.34 (m, 6 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.8 (d, *J* = 8.3 Hz), 135.5 (d, *J* = 5.3 Hz), 129.6 (d, *J* = 3.5 Hz), 125.2 (d, *J* = 11.5 Hz), 64.3 (d, *J* = 10.1 Hz), 16.1 (d, *J* = 11.5 Hz).

^{31}P NMR (160 MHz, $CDCl_3$): δ = 22.2.

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{10}H_{14}ClO_3PSNa$: 302.9982; found: 302.9980.

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Supporting Information

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