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# Peroxide promoted metal-free thiolation of phosphites by thiophenols/disulfides

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ABSTRACT

A metal-free oxidative P–S bonds coupling method for the synthesis of thiophosphates with DTBP as the oxidant is established. A wide range of functionalities are tolerated in the method. This method provides a facile way to synthesize thiophophates from readily available thiophenols/disulfides and phosphites.



## 1. Introduction

The formation of P–S bonds is one important tool in building sulfur-contained organophosphorus compounds. Among them, thiophosphates are prominent due to their promising biological activities and applications in agricultural industry.[1,2] Conventional strategies for the synthesis of thiophosphates often started with prefunctionalized substrates,[3] which usually included multiple steps and limited their applications. In the past year, the direct thiolation of phosphites using readily accessible sulfur source has made significant progress.[4] For example, Zhao and co-workers described an efficient copper iodide catalyzed P–S coupling reaction between disulfides and dialkyl phosphites.[4d] In 2014, an excellent thiophosphates synthesis work using thiols and dialkyl phosphites in the presence of *N*-chlorosuccinimide has been reported by Lee's group.[4f]

Recently, the direct functionalization of S–H bonds under oxidative conditions has received much attention.[5] This atom and step economy pathway has been applied in the synthesis of sulfur-contained compounds, such as in the C–S bonds building of thioesters.[6] In light of the precedent literature about phosphorous radicals and our research on thiol chemistry,[7,8] we designed an oxidative P–S bonds coupling reaction for the synthesis of thiophosphates, which exhibited several advantages, including the use of readily available substrates, high atom economy, and no use of any bases or acids. Herein, we report a metal-free oxidative coupling reaction between thiophenols (or disulfides) and phosphites using di-*tert*-butyl peroxide (DTBP) as oxidant.

## 2. Results and discussion

We started our investigation by introducing thiophenol (**1a**) and diethyl phosphite (**2a**) as the model substrates to optimize the reaction conditions. Initially, **1a** and **2a** were added to DMSO in the presence of TBHP and reacted at 60 °C for 20 h (Table 1, entry 1). Unfortunately, no desired product was detected. By elevating the temperature to 80 °C, product **3a** could be obtained in 62%. We then screened a wide range of the oxidant candidates, such as $H_2O_2$, TBPB, DTBP, $K_2S_2O_8$, and $(PhCOO)_2$ (entries 3–7), among them, DTBP was found to be the best choice, which furnished the desired product in 92% yield (entry 5). Besides, a decreased yield was found when the reaction was proceeded under air (entry 8). Furthermore, the solvents effect was studied. A variety of solvents, including dioxane, toluene, DMF, $H_2O$, and ethyl acetate were tested and all of them showed poor yields or not reacted at all (entries 9–13). On the other hand, increasing the reaction temperature to 100 °C or reducing the amount of oxidant (entries 14 and 15) slightly reduced the yields. Yet it was worth noting that, even without any oxidants, **3a** could be obtained in 21% yield, which could be ascribed to the weak oxidizability of DMSO.[9]

With the optimal reaction conditions in hand, the substrates scope of thiophenols was explored later. As shown in Scheme 1, a wide range of substituted thiophenols were subjected to our

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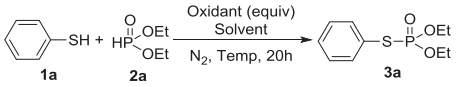
**Table 1**
Optimization of the reaction condition[a]




1a 2a 3a

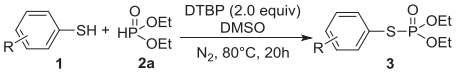
| Entry | Oxidant (equiv) | Solvent | $T$ (°C) | Yield[b] (%) |
|---|---|---|---|---|
| 1 | TBHP (2) | DMSO | 60 | N.D. |
| 2 | TBHP (2) | DMSO | 80 | 62 |
| 3 | $H_2O_2$ (2) | DMSO | 80 | 87 |
| 4 | TBPB (2) | DMSO | 80 | 86 |
| 5 | DTBP (2) | DMSO | 80 | 92 |
| 6 | $K_2S_2O_8$ (2) | DMSO | 80 | N.D. |
| 7 | $(PhCOO)_2$ (2) | DMSO | 80 | 29 |
| 8[c] | DTBP (2) | DMSO | 80 | 85 |
| 9 | DTBP (2) | Dioxane | 80 | 7 |
| 10 | DTBP (2) | Toluene | 80 | N.D. |
| 11 | DTBP (2) | DMF | 80 | 44 |
| 12 | DTBP (2) | $H_2O$ | 80 | N.D. |
| 13 | DTBP (2) | EtOAc | 80 | N.D. |
| 14 | DTBP (2) | DMSO | 100 | 83 |
| 15 | DTBP (1) | DMSO | 80 | 82 |
| 16 | | DMSO | 80 | 21 |

TBHP=*tert*-butyl hydroperoxide, DTBP=di-*tert*-butyl peroxide, TBPB=*tert*-butylperoxybenzoate.

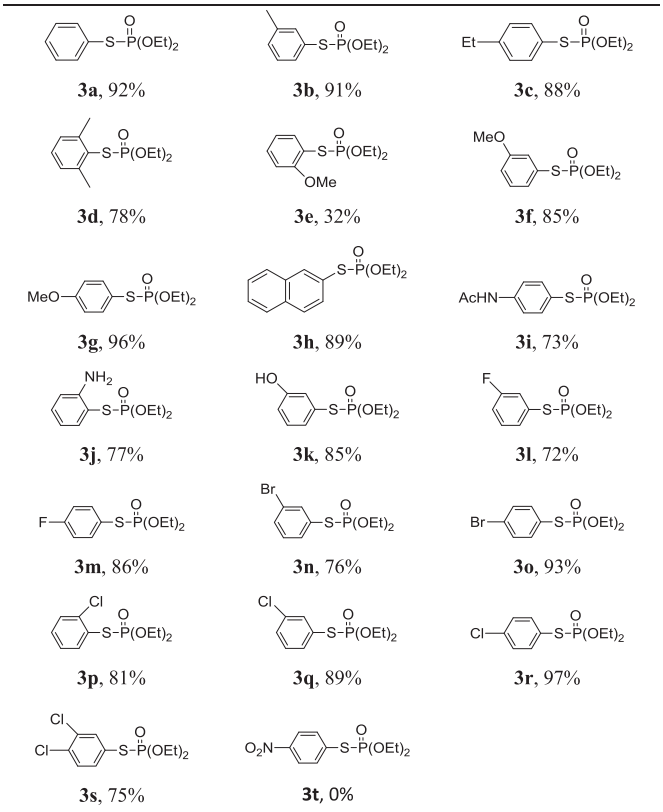
[a] Reaction conditions: thiophenol (1.0 mmol), diethyl phosphite (2.0 mmol), oxidant (2.0 mmol) were added in 2 mL solvent and heated under a nitrogen atmosphere for 20 h.

[b] Isolated yield.

[c] Reaction in air condition.




1 2a 3

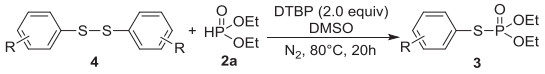



[a] Reaction conditions: **1** (1.0 mmol), **2a** (2.0 mmol), DTBP (2.0 mmol), DMSO (1.5 mL), at 80°C, under $N_2$ atmosphere for 20 h. Isolated yield.

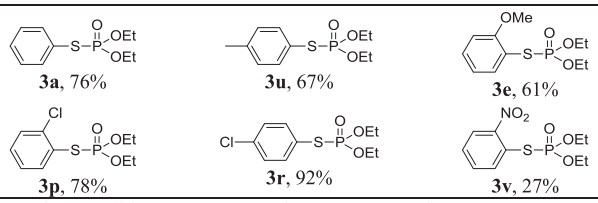
**Scheme 1.** Coupling of diethyl phosphite with substituted thiophenols.[a]

reaction conditions, and formed the corresponding thiophosphates in good to excellent yields. Functionalities including alkyl, MeO, AcNH, F, Br, Cl were well tolerated. To our delight, sensitive groups such as $NH_2$ and OH were well persevered under our oxidative conditions and gave good yields (**3j**, **3k**). Besides, thiophenols with single electron-donating or electron-withdrawing group showed no obvious differences in reactivity, for example, the yields of *meta*-/*para*-methoxy substituted thiophenols (entries **3f**, **3g**) are comparable to their chloro counterparts (**3q**, **3r**). However, for the thiophenol with double electron-withdrawing groups (entry **3s**), a reduced yield was found. Meanwhile, no desired product was formed when using nitro-substituted thiophenol as substrate (**3t**). Except for the electronic effect, steric effect also had a remarkable influence on this reaction. The *ortho*-substituted substrates (**3e**, **3p**) revealed less reactivity when compared with their *meta*- or *para*-analogs (**3f**, **3r**). And such effect could also be found in the highly substituted 2,6-dimethyl-benzenethiol (**3d**).

As we all know, disulfides were important sulfur source in building P–S bonds, which proved to be more stable and bearing less odor. Under this background, several disulfides substrates were then employed to our reaction. The result was summarized in Scheme 2. All disulfides were smoothly reacted with diethyl phosphite and most of them afforded the corresponding thiophosphates with moderate to good yields. It could be found that electron-withdrawing group such as chloro (**3p**, **3r**) facilitated our reaction, while disulfides with electron-donating groups (**3u**, **3e**) showed lower reactivity. Furthermore, disulfide that bearing strong electron-withdraw group ($NO_2$) could also be transformed to the corresponding product (**3v**) though in low yield. Besides, steric hindrance also exhibited significant influence. A reduced yield was found in the case (**3p**) of *ortho*-substituted thiophosphate in contrast to its related *para* product (**3r**).




4 2a 3

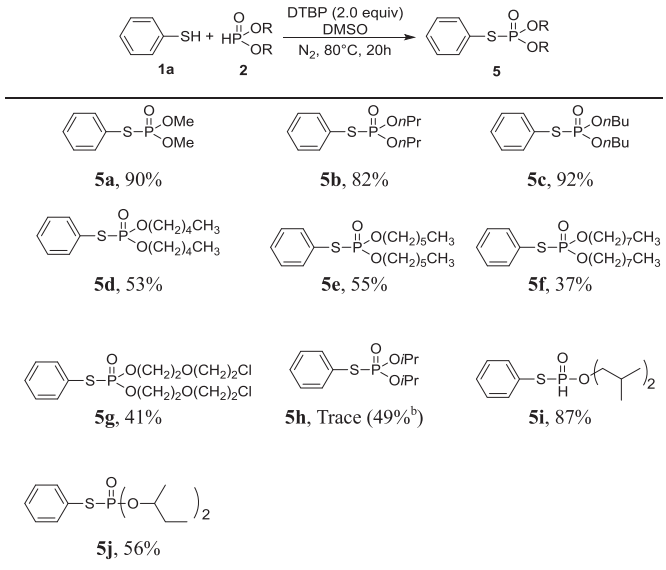



[a] Reaction conditions: **4** (0.5 mmol), **2a** (2.0 mmol), DTBP (2.0 mmol), DMSO (1.5 mL), at 80°C, under $N_2$ atmosphere for 20 h. Isolated yield.

**Scheme 2.** Coupling of diethyl phosphite with substituted disulfides.[a]

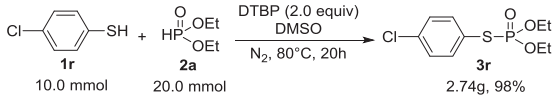
To further explore the substrate scope, reactions between thiophenols and a range of dialkyl phosphites were also examined. As depicted in Scheme 3, dialkyl phosphites with different alkyl chains could be successfully converted to the related thiophosphates with yields from 37% to 92%. Notably, variation of the chain length in the dialkyl phosphite substrates significantly affected the reactivity. When the straight carbon chains increased, an obvious trend of decrease in yield was found (**5a**–**5g**). Besides, due to the steric effect, dialkyl phosphites with branched chains (**5h**–**5j**) showed lower yields when compared with their straight chain homologs (**5b**,**5c**). For example, under our standard conditions, only traceable **5h** could be obtained (Instead of DTBP, incorporating $H_2O_2$ as the oxidant could improve the yield to 49%.).

Subsequently, a scale-up reaction was conducted to demonstrate the utility of this DTBP promoted P–S bonds coupling reaction. As shown in Scheme 4, under the standard conditions, 2.80 g (10.0 mmol) of **1r** could be converted to **3r** in 98% yield.



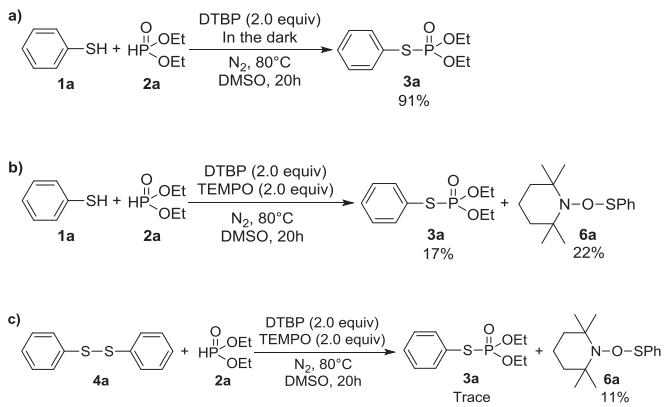

[a]Reaction conditions: **1a** (1.0 mmol), **2** (2.0 mmol), DTBP (2.0 mmol), DMSO (1.5 mL), at 80°C, under $N_2$ atmosphere for 20 h. Isolated yield. [b]Using $H_2O_2$ as oxidant.

**Scheme 3.** Coupling of dialkyl phosphites with thiophenol.[a]



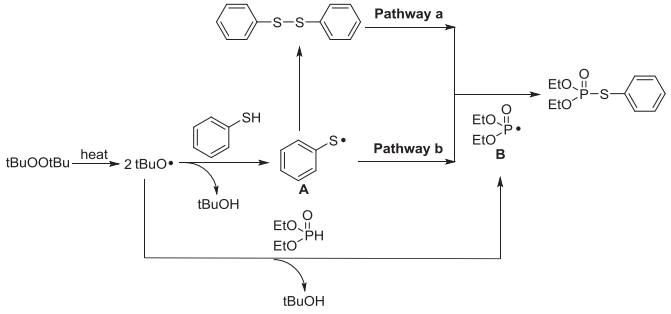

**Scheme 4.** Gram-scale reaction.

On the basis of precedent reports and the following control experiments,[6f,7g,10] a preliminary mechanism study for the DTBP promoted P–S bond coupling reaction was conducted. As depicted in Scheme 5, when performed in the dark, the product **3a** could also be obtained in 91% yield, which implied that a photoirradiation process was not involved. Then, the radical inhibitor (TEMPO) was incorporated under our optimal reaction conditions. For thiophenol (**1a**) substrate, a great reduction in yield was found (17%). And TEMPO could even block this reaction when using disulfide (**4a**) as substrate. Besides, in both control experiments, thiyl radical (PhS•) was captured by TEMPO and afforded **6a**, which is the strong evidence that a radical pathway may be involved.




**Scheme 5.** Control experiments.

Based on the above information, a plausible reaction mechanism was proposed and presented in Scheme 6. Firstly, the *tert*-butoxy radical was generated by homo-cleavage of DTBP. The *tert*-butoxy radical then reacted with thiophenol and diethyl phosphite, respectively, furnished the thiyl radical **A** and phosphorus radical **B**. The former radical quickly formed disulfide by self-coupling, then reacted with the phosphorus radical **B** through a substitution process (pathway a) or directly added to radical **B** (pathway b) to afford the product.




**Scheme 6.** Plausible mechanism.

## 3. Conclusions

In summary, we have developed a DTBP promoted direct P–S bonds coupling reaction by utilizing simple thiophenols/disulfides and dialkyl phosphites as substrates. The metal-free method has exhibited a good functional compatibility, substituents such as bromo, chloro, fluoro, amino, and hydroxyl were well tolerated in our reaction conditions. Additionally, dialkyl phosphites with different chains were suitable substrates for our reaction. In all, our reaction has provided a more attractive pathway for the synthesis of biological and agricultural useful thiophosphate compounds.

## 4. Experimental section

### 4.1. General information

Reagents and solvents were purchased from commercial suppliers and used without additional purification. Some dialkyl phosphites substrates were synthesized according to the former report.[11] $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker ARX-400. High-resolution mass spectra were performed on a TOF-MS instrument with an ESI source. Melting points were measured on SGW.X-4 (uncorrected).

### 4.2. General procedure of the coupling between thiophenol/substituted thiophenols and dialkyl phosphites (3a–3t, 5a–5j)

A Schlenk tube was charged with thiophenol **1** (1.0 mmol), dialkyl phosphites **2** (2.0 mmol), and DTBP (2.0 mmol), then 1.5 mL DMSO was added as solvent. This reaction was performed under $N_2$ atmosphere at 80 °C for 20 h. After completion of the reaction, the mixture was quenched with 20 mL $Na_2S_2O_4$ solution (5%) then extracted with ethyl acetate (15 mL×3). The organic layer was combined and dried with anhydrous $Na_2SO_4$. After the evaporation in a vacuum, the crude product was purified by a gel column chromatography using petroleum ether/ethyl acetate as eluent to afford the desired products **3** and **5**.

*4.2.1. Thiophosphoric acid O,O′-diethyl ester S-phenyl ester (**3a**).* Colorless oil. Yield: 226.3 mg (92%). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.55–7.52 (m, 2H), 7.33–7.31 (m, 3H), 4.23–4.08 (m,

4H), 1.29–1.25 (m, 6H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 134.5 (d, $J$=5.0 Hz), 129.3 (d, $J$=2.3 Hz), 129.0 (d, $J$=2.8 Hz), 126.6 (d, $J$=7.0 Hz), 64.1 (d, $J$=6.13 Hz), 16.0 (d, $J$=7.2 Hz); $^{31}$P NMR ($CDCl_3$, 162 MHz): $\delta$ 22.9; IR (neat): 3454, 2966, 1473, 1441, 1254, 1011, 747, 602 cm$^{-1}$; HRMS (ESI-TOF) $m/z$ calcd for $C_{10}H_{16}O_3PS$ $[M+H]^+$ 247.0558, found 247.0557.

*4.2.2. Thiophosphoric acid O,O′-diethyl ester S-m-tolyl ester (**3b**).* Colorless oil. Yield: 236.0 mg (91%). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.33 (m, 2H), 7.20 (m, 1H), 7.13 (d, $J$=7.6 Hz, 1H), 4.23–4.09 (m, 4H), 2.31 (s, 3H), 1.28 (m, 6H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 139.2 (d, $J$=2.3 Hz), 135.1 (d, $J$=5.2 Hz), 131.5 (d, $J$=5.2 Hz), 129.8 (d, $J$=2.9 Hz), 129.1 (d, $J$=2.3 Hz), 126.0 (d, $J$=7.2 Hz), 64.0 (d, $J$=6.1 Hz), 21.2, 16.0 (d, $J$=7.3 Hz); $^{31}$P NMR ($CDCl_3$, 162 MHz): $\delta$ 22.7; IR (neat): 3492, 2984, 1592, 1475, 1391, 1255, 1162, 1015, 974, 783, 690 cm$^{-1}$; HRMS (ESI-TOF) $m/z$ calcd for $C_{11}H_{18}O_3PS$ $[M+H]^+$ 261.0714, found 261.0719.

*4.2.3. Thiophosphoric acid O,O′-diethyl ester S-(4-ethyl-phenyl) ester (**3c**).* Colorless oil. Yield: 241.6 mg (88%). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.44–7.42 (d, $J$=8.2 Hz, 2H), 7.15–7.13 (d, $J$=8.0 Hz, 2H), 4.23–4.08 (m, 4H), 2.63–2.58 (m, 2H), 1.29–1.25 (t, $J$=7.1 Hz, 6H), 1.21–1.17 (m, 3H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 145.5 (d, $J$=3.1 Hz), 134.7 (d, $J$=5.1 Hz), 128.9 (d, $J$=2.4 Hz), 123.0 (d, $J$=7.2 Hz), 64.0 (d, $J$=6.13 Hz), 28.5, 16.0 (d, $J$=7.2 Hz), 15.3; $^{31}$P NMR ($CDCl_3$, 162 MHz): $\delta$ 23.4; IR (neat): 3454, 2969, 1477, 1391, 1254, 1161, 1014, 973, 828, 790, 600 cm$^{-1}$; HRMS (ESI-TOF) $m/z$ calcd for $C_{12}H_20O_3PS$ $[M+H]^+$ 275.0871; found 275.0874.

*4.2.4. Thiophosphoric acid S-(2,6-dimethyl-phenyl) ester O,O′-diethyl ester (**3d**).* Colorless oil. Yield: 213.6 mg (78%). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.18–7.10 (m, 3H), 4.16–4.05 (m, 4H), 2.58 (s, 6H), 1.29–1.25 (m, 3H); $^{13}$C NMR: ($CDCl_3$, 100 MHz) $\delta$ 143.3 (d, $J$=4.7 Hz), 129.4 (d, $J$=3.6 Hz), 128.4 (d, $J$=3.2 Hz), 124.8 (d, $J$=7.9 Hz), 64.2 (d, $J$=7.3 Hz), 22.5, 16.1 (d, $J$=6.8 Hz); $^{31}$P NMR ($CDCl_3$, 162 MHz): $\delta$ 23.1; IR (neat): 3489, 3056, 2982, 2930, 2736, 1939, 1774, 1630, 1460, 1390, 1252, 1163, 1016, 968, 774, 605 cm$^{-1}$; HRMS (ESI-TOF) $m/z$ calcd for $C_{12}H_{20}O_3PS$ $[M+H]^+$ 275.0871; found 275.0872.

*4.2.5. Thiophosphoric acid O,O′-diethyl ester S-(2-methoxy-phenyl) ester (**3e**).* Colorless oil. Yield: 88.3 mg (32%). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.58–7.55 (m, 1H), 7.33–7.23 (m, 1H), 6.93–6.87 (m, 2H), 4.26–4.12 (m, 4H), 3.86 (s, 3H), 1.29–1.26 (m, 6H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 159.4 (d, $J$=7.9 Hz), 136.9 (d, $J$=4.4 Hz), 130.9 (d, $J$=2.9 Hz), 121.3 (d, $J$=2.5 Hz), 114.5 (d, $J$=7.1 Hz), 114.4 (d, $J$=10.0 Hz), 63.8 (d, $J$=5.7 Hz), 55.8; 16.0 (d, $J$=7.6 Hz); $^{31}$P NMR ($CDCl_3$, 162 MHz): $\delta$ 22.9; IR (neat): 3442, 2984, 2939, 2415, 1639, 1583, 1479, 1392, 1250, 1018, 977, 795, 755, 575 cm$^{-1}$; HRMS (ESI-TOF) $m/z$ calcd for $C_{11}H_{18}O_4PS$ $[M+H]^+$ 277.0663, found 277.0667.

*4.2.6. Thiophosphoric acid O,O′-diethyl ester S-(3-methoxy-phenyl) ester (**3f**).* Colorless oil. Yield: 234.8 mg (85%). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.27–7.25 (m, 1H), 7.15–7.12 (m, 2H), 6.91–6.89 (m, 1H), 4.26–4.13 (m, 4H), 3.81 (s, 3H), 1.33–1.30 (m, 6H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 159.8 (d, $J$=2.1 Hz), 130.0 (d, $J$=2.2 Hz), 127.4 (d, $J$=6.9 Hz), 126.6 (d, $J$=5.5 Hz), 119.6 (d, $J$=5.2 Hz), 115.0 (d, $J$=2.6 Hz), 64.1 (d, $J$=6.2 Hz), 55.3, 16.0 (d, $J$=7.2 Hz); $^{31}$P NMR ($CDCl_3$, 162 MHz): $\delta$ 22.8; IR (neat): 3490, 2984, 2938, 2070, 1590, 1478, 1250, 1161, 1013, 973, 857, 788, 687, 606 cm$^{-1}$; HRMS (ESI-TOF) $m/z$ calcd for $C_{11}H_{18}O_4PS$ $[M+H]^+$ 277.0663, found 277.0665.

*4.2.7. Thiophosphoric acid O,O′-diethyl ester S-(4-methoxy-phenyl) ester (**3g**).* Colorless oil. Yield: 265.1 mg (96%). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.45–7.43 (m, 2H), 6.85–6.83 (m, 2H), 4.19–4.10 (m, 4H), 3.77 (s, 3H), 1.29–1.26 (m, 6H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 160.5 (d, $J$=2.9 Hz), 136.4 (d, $J$=4.7 Hz), 116.6 (d, $J$=7.4 Hz), 115.0 (d, $J$=2.3 Hz), 64.0 (d, $J$=6.2 Hz), 55.4, 16.1 (d, $J$=7.1 Hz); $^{31}$P NMR ($CDCl_3$, 162 MHz): $\delta$ 23.6; IR (neat): 3463, 2983, 1592, 1494, 1289, 1249, 1162, 1015, 974, 829, 603 cm$^{-1}$; HRMS (ESI-TOF) $m/z$ calcd for $C_{11}H_{18}O_4PS$ $[M+H]^+$ 277.0663, found 277.0671.

*4.2.8. Thiophosphoric acid O,O′-diethyl ester S-naphthalen-2-yl ester (**3h**).* Colorless oil. Yield: 263.1 mg (89%). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 8.06 (s, 1H), 7.82–7.77 (m, 3H), 7.60–7.57 (m, 1H), 7.51–7.47 (m, 2H), 4.27–4.12 (m, 4H), 1.30–1.27 (m, 6H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 134.4 (d, $J$=6.7 Hz), 133.6 (d, $J$=2.4 Hz), 133.1 (d, $J$=1.9 Hz), 130.9 (d, $J$=4.0 Hz), 129.0 (d, $J$=1.59 Hz), 127.7 (d, $J$=1.2 Hz), 127.7 (d, $J$=0.85 Hz), 127.0 (d, $J$=1.08 Hz), 126.7, 123.8 (d, $J$=7.4 Hz), 64.2 (d, $J$=6.2 Hz), 16.0 (d, $J$=7.1 Hz); $^{31}$P NMR ($CDCl_3$, 162 MHz): $\delta$ 22.9; IR (neat): 3490, 3054, 2984, 2906, 1625, 1588, 1500, 1391, 1247, 1161, 1014, 941, 860, 816, 747, 602 cm$^{-1}$; HRMS (ESI-TOF) $m/z$ calcd for $C_{14}H_{18}O_3PS$ $[M+H]^+$ 297.0714, found 297.0719.

*4.2.9. Thiophosphoric acid S-(4-acetylamino-phenyl) ester O,O′-diethyl ester (**3i**).* White solid, mp: 132–133 °C. Yield: 221.4 mg (73%). $^1$H NMR (DMSO-$d_6$, 400 Hz): $\delta$ 10.13 (s, 1H), 7.63 (m, 2H), 7.47 (m, 2H), 4.21–4.02 (m, 2H), 2.06 (s, 3H), 1.21 (m, 6H); $^{13}$C NMR (DMSO-$d_6$, 100 MHz): $\delta$ 168.6, 140.3 (d, $J$=2.9 Hz), 135.3 (d, $J$=4.7 Hz), 119.6 (d, $J$=2.0 Hz), 118.5 (d, $J$=7.2 Hz), 63.6 (d, $J$=6.1 Hz), 39.8, 39.6, 39.4, 39.2, 23.9, 15.7 (d, $J$=6.9 Hz); $^{31}$P NMR (DMSO-$d_6$, 162 MHz): $\delta$ 21.8; IR (KBr): 3303, 2985, 1901, 1668, 1591, 1536, 1396, 1317, 1239, 1014, 969, 815, 747, 605 cm$^{-1}$; HRMS (ESI-TOF) $m/z$ calcd for $C_{12}H_{19}NO_4PS$ $[M+H]^+$ 304.0772, found 304.0783.

*4.2.10. Thiophosphoric acid S-(2-amino-phenyl) ester O,O′-diethyl ester (**3j**).* Colorless oil. Yield: 201.2 mg (77%). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.37–7.35 (m, 1H), 7.16–7.12 (m, 1H), 6.75–6.66 (m, 2H), 4.19–4.08 (m, 4H), 3.73 (br, 2H), 1.29–1.25 (m, 6H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 149.1, 137.5 (d, $J$=4.2 Hz), 131.2 (d, $J$=3.2 Hz), 119.0 (d, $J$=2.6 Hz), 116.2 (d, $J$=2.6 Hz), 108.4 (d, $J$=7.5 Hz), 64.5 (d, $J$=6.9 Hz), 16.1 (d, $J$=6.9 Hz); $^{31}$P NMR ($CDCl_3$, 162 MHz): $\delta$ 22.8; IR (neat): 3345, 2982, 1615, 1479, 1392, 1297, 1209, 1099, 818, 752, 549 cm$^{-1}$; HRMS (ESI-TOF) $m/z$ calcd for $C_{10}H_{17}NO_3PS$ $[M+H]^+$ 262.0667, found 263.0669.

*4.2.11. Thiophosphoric acid O,O′-diethyl ester S-(3-hydroxy-phenyl) ester (**3k**).* Colorless oil. Yield: 222.7 mg (85%); $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.12–7.08 (m, 2H), 6.99–6.97 (m, 1H), 6.77–6.75 (m, 1H), 4.24–4.10 (m, 4H), 1.31–1.28 (m, 6H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 157.5 (d, $J$=2.0 Hz), 125.9 (d, $J$=2.4 Hz), 125.7 (d, $J$=5.5 Hz), 121.9 (d, $J$=6.9 Hz), 116.9 (d, $J$=5.0 Hz), 64.6 (d, $J$=6.6 Hz), 16.0 (d, $J$=7.1 Hz); $^{31}$P NMR ($CDCl_3$, 162 MHz): $\delta$ 20.8; IR (neat): 3228, 2986, 2926, 1583, 1475, 1443, 1219, 1160, 1219, 1014, 978, 885, 609 cm$^{-1}$; HRMS (ESI-TOF) $m/z$ calcd for $C_{10}H_{16}O_4PS$ $[M+H]^+$ 263.0507, found 263.0507.

*4.2.12. Thiophosphoric acid O,O′-diethyl ester S-(3-fluoro-phenyl) ester (**3l**).* Colorless oil. Yield: 190 mg (72%). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.34–7.26 (m, 3H), 7.07–7.01 (m, 1H), 4.25–4.10 (m, 4H), 1.31–1.27 (m, 6H); $^{13}$C NMR ($CDCl_3$, 100 MHz): $\delta$ 163.7 (d, $J$=2.2 Hz), 161.2 (d, $J$=2.3 Hz), 130.5 (dd, $J_1$=8.2 Hz, $J_2$=2.1 Hz), 130 (dd, $J_1$=5.6 Hz, $J_2$=3.2 Hz), 128.6 (t, $J$=7.8 Hz), 121.4 (dd, $J_1$=22.7 Hz, $J_2$=5.2 Hz), 116.3 (dd, $J_1$=20.1 Hz, $J_2$=2.6 Hz), 64.3 (d, $J$=6.2 Hz), 16.0 (d, $J$=7.1 Hz); $^{31}$P NMR ($CDCl_3$, 162 MHz): $\delta$ 21.9; IR (neat): 3494, 3070, 2986, 1581, 1474, 1422, 1251, 1161, 1048, 976, 876, 786, 682, 603 cm$^{-1}$; HRMS (ESI-TOF) $m/z$ calcd for $C_{10}H_{15}FO_3PS$ $[M+H]^+$ 265.0464, found 265.0468.

*4.2.13. Thiophosphoric acid O,O′-diethyl ester S-(4-fluoro-phenyl) ester (**3m**).* Colorless oil. Yield: 227 mg (86%). $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 7.54–7.50 (m, 2H), 7.04–7.00 (m, 2H), 4.23–4.08 (m,

4H), 1.30–1.26 (m, 6H); $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ 164.6 (dd, $J_1$=248 Hz, $J_2$=3.2 Hz), 136.7 (dd, $J_1$=8.5 Hz, $J_2$=5.3 Hz), 121.7 (dd, $J_1$=7.3 Hz, $J_2$=3.5 Hz), 116.7 (dd, $J_1$=22.0 Hz, $J_2$=2.4 Hz), 64.2 (d, $J$=6.3 Hz), 16.0 (d, $J$=7.1 Hz); $^{31}P$ NMR ($CDCl_3$, 162 MHz): $\delta$ 22.6; IR (neat): 3491, 2985, 2908, 1589, 1490, 1393, 1255, 1159, 1014, 976, 835, 791, 601 $cm^{-1}$; HRMS (ESI-TOF) $m/z$ calcd for $C_{10}H_{15}FO_3PS$ $[M+H]^+$ 265.0464, found 265.0463.

*4.2.14. Thiophosphoric acid S-(3-bromo-phenyl) ester O,O′-diethyl ester (**3n**).* Colorless oil. Yield: 245.5 mg (76%). $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 7.69 (m, 1H), 7.50–7.44 (m, 2H), 7.21–7.17 (m, 1H), 4.26–4.07 (m, 4H), 1.30 (m, 6H); $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ 136.9 (d, $J$=5.4 Hz), 133.0 (d, $J$=5.2 Hz), 132.1 (d, $J$=2.8 Hz), 130.5 (d, $J$=2.2 Hz), 128.8 (d, $J$=7.2 Hz), 122.7 (d, $J$=2.6 Hz), 64.3 (d, $J$=6.3 Hz), 16.0 (d, $J$=7.2 Hz); $^{31}P$ NMR ($CDCl_3$, 162 MHz): $\delta$ 21.8; IR (neat): 3491, 3058, 2984, 2906, 1764, 1573, 1459, 1395, 1258, 1162, 1013, 975, 877, 783, 748, 600 $cm^{-1}$; HRMS (ESI-TOF) $m/z$ calcd for $C_{10}H_{15}BrO_3PS$ $[M+H]^+$ 324.9663, found 324.9660.

*4.2.15. Thiophosphoric acid S-(4-bromo-phenyl) ester O,O′-diethyl ester (**3o**).* Colorless oil. Yield: 301 mg (93%). $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 7.49–7.42 (m, 2H), 7.45–7.42 (m, 2H), 4.27–4.11 (m, 4H), 1.34–1.30 (m, 6H); $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ 136.0 (d, $J$=5.18 Hz), 132.5 (d, $J$=2.2 Hz), 125.8 (d, $J$=7.2 Hz), 123.7 (d, $J$=3.5 Hz), 64.3 (d, $J$=6.3 Hz), 16.0 (d, $J$=7.0 Hz); $^{31}P$ NMR ($CDCl_3$, 162 MHz): $\delta$ 21.9; IR (neat): 3492, 3082, 2984, 2906, 1901, 1634, 1565, 1388, 1257, 1162, 1087, 1008, 975, 817, 753, 600 $cm^{-1}$; HRMS (ESI-TOF) $m/z$ calcd for $C_{10}H_{15}BrO_3PS$ $[M+H]^+$ 324.9663, found 324.9660.

*4.2.16. Thiophosphoric acid S-(2-chloro-phenyl) ester O,O′-diethyl ester (**3p**).* Colorless oil. Yield: 227 mg (81%). $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 7.73–7.70 (m, 1H), 7.43–7.40 (m, 1H), 7.28–7.19 (m, 2H), 4.26–4.08 (m, 4H), 1.30–1.26 (m, 6H); $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ 137.9 (d, $J$=6.9 Hz), 136.8 (d, $J$=4.4 Hz), 130.3 (d, $J$=2.7 Hz), 130.2 (d, $J$=2.3 Hz), 127.4 (d, $J$=2.3 Hz), 126.3 (d, $J$=6.8 Hz), 64.4 (d, $J$=6.2 Hz), 16.0 (d, $J$=7.3 Hz); $^{31}P$ NMR ($CDCl_3$, 162 MHz): $\delta$ 21.3; IR (neat): 3493, 2984, 2907, 1631, 1453, 1391, 1255, 1162, 1015, 976, 756, 599 $cm^{-1}$; HRMS (ESI-TOF) $m/z$ calcd for $C_{10}H_{15}ClO_3PS$ $[M+H]^+$ 281.0168, found 281.0168.

*4.2.17. Thiophosphoric acid S-(3-chloro-phenyl) ester O,O′-diethyl ester (**3q**).* Colorless oil. Yield: 249 mg (89%). $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 7.54–7.53 (m, 1H), 7.45–7.42 (m, 1H), 7.33–7.30 (m, 1H), 7.27–7.25 (m, 1H), 4.25–4.10 (m, 4H), 1.31–1.28 (m, 6H); $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ 134.8 (d, $J$=2.5 Hz), 134.1 (d, $J$=5.4 Hz), 132.5 (d, $J$=5.2 Hz), 130.3 (d, $J$=2.2 Hz), 129.2 (d, $J$=2.7 Hz), 128.5 (d, $J$=7.0 Hz), 64.3 (d, $J$=6.2 Hz), 16.0 (d, $J$=7.1 Hz); $^{31}P$ NMR ($CDCl_3$, 162 MHz): $\delta$ 21.8; IR (neat): 3475, 2984, 1574, 1461, 1401, 1256, 1162, 1013, 777, 680, 600 $cm^{-1}$; HRMS (ESI-TOF) $m/z$ calcd for $C_{10}H_{15}ClO_3PS$ $[M+H]^+$ 281.0168, found 281.0166.

*4.2.18. Thiophosphoric acid S-(4-chloro-phenyl) ester O,O′-diethyl ester (**3r**).* Colorless oil. Yield: 288 mg (97%). $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 7.48–7.46 (m, 2H), 7.30–7.29 (m, 2H), 4.23–4.09 (m, 4H), 1.30–1.27 (m, 6H); $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ 135.7 (d, $J$=5.2 Hz), 135.5 (d, $J$=3.4 Hz), 129.5 (d, $J$=2.3 Hz), 125.1 (d, $J$=3.3 Hz), 64.2 (d, $J$=6.3 Hz), 16.0 (d, $J$=7.1 Hz); $^{31}P$ NMR ($CDCl_3$, 162 MHz): $\delta$ 22.1; IR (neat): 3492, 3064, 2984, 2932, 1639, 1572, 1476, 1443, 1391, 1254, 1091, 1013, 822, 791, 600 $cm^{-1}$; HRMS (ESI-TOF) $m/z$ calcd for $C_{10}H_{15}ClO_3PS$ $[M+H]^+$ 281.0168, found 281.0166.

*4.2.19. Thiophosphoric acid S-(3,4-dichloro-phenyl) ester O,O′-diethyl ester (**3s**).* Colorless oil. Yield: 234.1 mg (75%). $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 7.62 (s, 1H), 7.38 (m, 1H), 4.25–4.09 (m, 4H), 1.32–1.28 (m, 6H); $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ 135.8 (d, $J$=5.4 Hz), 133.8 (d, $J$=3.3 Hz), 133.6 (d, $J$=5.1 Hz), 133.2 (d, $J$=2.5 Hz), 131.0 (d, $J$=2.2 Hz), 126.7 (d, $J$=7.1 Hz), 64.5 (d, $J$=6.4 Hz), 16.0 (d, $J$=7.0 Hz); $^{31}P$ NMR ($CDCl_3$, 162 MHz): $\delta$ 21.3; IR (neat): 2455, 2985, 1630, 1476, 1366, 1258, 1162, 1012, 976, 810, 602 $cm^{-1}$; HRMS (ESI-TOF) $m/z$ calcd for $C_{10}H_{14}Cl_2O_3PS$ $[M+H]^+$ 314.9778, found 314.9786.

*4.2.20. Thiophosphoric acid O,O′-dimethyl ester S-phenyl ester (**5a**).* Colorless oil. Yield: 196 mg (90%). $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 7.54–7.51 (m, 2H), 7.33–7.32 (m, 3H), 3.80 (s, 3H), 3.77 (s, 3H); $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ 134.6 (d, $J$=5.2 Hz), 129.5 (d, $J$=2.3 Hz), 129.2 (d, $J$=2.9 Hz), 125.9 (d, $J$=7.2 Hz), 54.2 (d, $J$=6.1 Hz); $^{31}P$ NMR ($CDCl_3$, 162 MHz): $\delta$ 26.2; IR (neat): 3455, 2954, 1712, 1640, 1474, 1441, 1257, 1181, 1020, 830, 795, 691, 600 $cm^{-1}$; HRMS (ESI-TOF) $m/z$ calcd for $C_8H_{12}O_3PS$ $[M+H]^+$ 219.0245, found 219.0246.

*4.2.21. Thiophosphoric acid S-phenyl ester O,O′-dipropyl ester (**5b**).* Colorless oil. Yield: 225 mg (82%). $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 7.55 (m, 2H), 7.38–7.27 (m, 3H), 4.14–3.95 (m, 4H), 1.65 (m, 4H), 0.88 (m, 6H); $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ 134.5 (d, $J$=5.3 Hz), 129.3 (d, $J$=2.1 Hz), 128.9 (d, $J$=2.7 Hz), 126.6 (d, $J$=7.1 Hz), 69.5 (d, $J$=6.7 Hz), 23.5 (d, $J$=7.2 Hz), 9.9; $^{31}P$ NMR ($CDCl_3$, 162 MHz): $\delta$ 22.7; IR (neat): 3451, 2969, 1640, 1473, 1440, 1260, 1052, 994, 748, 602 $cm^{-1}$; HRMS (ESI-TOF) $m/z$ calcd for $C_{12}H_{20}O_3PS$ $[M+H]^+$ 275.0871, found 275.0870.

*4.2.22. Thiophosphoric acid O,O′-dibutyl ester S-phenyl ester (**5c**).* Colorless oil. Yield: 278 mg (92%). $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 7.63–7.52 (m, 2H), 7.35 (m, 3H), 4.21–4.02 (m, 4H), 1.67–1.57 (m, 4H), 1.42–1.29 (m, 4H), 0.91–0.88 (m, 6H); $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ 134.5 (d, $J$=5.3 Hz), 129.3 (d, $J$=2.1 Hz), 128.9 (d, $J$=2.8 Hz), 126.6 (d, $J$=7.1 Hz), 67.7 (d, $J$=6.7 Hz), 32.1 (d, $J$=7.2 Hz), 18.6, 13.5; $^{31}P$ NMR ($CDCl_3$, 162 MHz): $\delta$ 22.9; IR (neat): 3489, 3060, 2960, 2873, 1631, 1581, 1471, 1383, 1258, 1021, 987, 900, 758, 747, 692, 603 $cm^{-1}$; HRMS (ESI-TOF) $m/z$ calcd for $C_{14}H_{24}O_3PS$ $[M+H]^+$ 303.1184, found 303.1184.

*4.2.23. Thiophosphoric acid O,O′-dipentyl ester S-phenyl ester (**5d**).* Colorless oil. Yield: 175 mg (53%). $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 7.55 (m, 2H), 7.41–7.27 (m, 3H), 4.14–4.02 (m, 4H), 1.67–1.56 (m, 4H), 1.33–1.23 (m, 8H), 0.86 (m, 6H); $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ 134.4 (d, $J$=5.3 Hz), 129.3 (d, $J$=2.0 Hz), 128.9 (d, $J$=2.7 Hz), 126.7 (d, $J$=7.0 Hz), 68.1 (d, $J$=6.6 Hz), 29.84 (d, $J$=7.1 Hz), 27.5, 22.1, 13.9; $^{31}P$ NMR ($CDCl_3$, 162 MHz): $\delta$ 22.9; IR (neat): 3490, 3061, 2958, 2871, 1582, 1441, 1381, 1260, 1044, 990, 831, 690, 603 $cm^{-1}$; HRMS (ESI-TOF) $m/z$ calcd for $C_{16}H_{28}O_3PS$ $[M+H]^+$ 331.1497, found 331.1501.

*4.2.24. Thiophosphoric acid O,O′-dihexyl ester S-phenyl ester (**5e**).* Colorless oil. Yield: 197 mg (55%). $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 7.58–7.55 (m, 2H), 7.39–7.29 (m, 3H), 4.16–4.10 (m, 4H), 1.71–1.60 (m, 4H), 1.34–1.22 (m, 12H), 0.89–0.86 (m, 6H); $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ 134.4 (d, $J$=5.3 Hz), 129.3 (d, $J$=2.0 Hz), 128.9 (d, $J$=2.7 Hz), 126.7 (d, $J$=7.0 Hz), 68.1 (d, $J$=6.7 Hz), 31.3 (d, $J$=6.6 Hz), 30.1 (d, $J$=7.2 Hz), 25.1 (d, $J$=4.0 Hz), 22.5 (d, $J$=4.2 Hz), 13.9; $^{31}P$ NMR ($CDCl_3$, 162 MHz): $\delta$ 22.9; IR (neat): 2474, 3061, 2957, 2930, 2859, 1468, 1257, 994, 746, 690, 603 $cm^{-1}$; HRMS (ESI-TOF) $m/z$ calcd for $C_{18}H_{32}O_3PS$ $[M+H]^+$ 359.1810, found 359.1819.

*4.2.25. Thiophosphoric acid O,O′-dioctyl ester S-phenyl ester (**5f**).* Colorless oil. Yield: 153 mg (37%). $^1H$ NMR ($CDCl_3$, 400 MHz): $\delta$ 7.55–7.53 (M, 2H), 7.37–7.28 (m, 3H), 4.16–4.01 (m, 4H), 1.65–1.57 (m, 4H), 1.33–1.17 (m, 20H), 0.86 (m, 6H); $^{13}C$ NMR ($CDCl_3$, 100 MHz): $\delta$ 134.4 (d, $J$=5.3 Hz), 129.3 (d, $J$=2.0 Hz), 128.9 (d, $J$=2.7 Hz), 126.7 (d, $J$=7.1 Hz), 68.1 (d, $J$=6.7 Hz), 31.7, 30.1 (d, $J$=7.1 Hz), 29.1 (d, $J$=9.3 Hz), 25.4, 22.6, 14.1; $^{31}P$ NMR ($CDCl_3$, 162 MHz): $\delta$ 22.9; IR (neat): 3473, 3061, 2926, 2855, 1582, 1467,

1378, 1261, 996, 746, 689, 603 $cm^{-1}$; HRMS (ESI-TOF) *m/z* calcd for $C_{22}H_{40}O_3PS$ $[M+H]^+$ 415.2436, found 415.2450.

*4.2.26. Thiophosphoric acid O,O′-bis-[2-(2-chloro-ethoxy)-ethyl] ester S-phenyl ester (**5g**).* Colorless oil. Yield: 165 mg (41%). $^1H$ NMR ($CDCl_3$, 400 MHz): δ 7.60–7.58 (m, 2H), 7.34–7.32 (m, 3H), 4.29–4.20 (m, 4H), 3.67–3.66 (m, 8H), 3.57–3.55 (m, 4H); $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ 134.7 (d, *J*=5.3 Hz), 129.4 (d, *J*=2.3 Hz), 129.2 (d, *J*=2.9 Hz), 125.9 (d, *J*=7.2 Hz), 71.3, 69.8 (d, *J*=7.4 Hz), 66.8 (d, *J*=6.5 Hz), 42.7; $^{31}P$ NMR ($CDCl_3$, 162 MHz): δ 24.1; IR (neat): 3456, 3060, 2958, 2871, 1631, 1581, 1473, 1299, 1256, 1135, 1024, 749, 665, 606 $cm^{-1}$; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{22}Cl_2O_5PS$ $[M+H]^+$ 403.0303, found 403.0313.

*4.2.27. Thiophosphoric acid O,O′-diisopropyl ester S-phenyl ester (**5h**).* Colorless oil. Yield: 134 mg (49%). $^1H$ NMR ($CDCl_3$, 400 MHz): δ 7.61–7.51 (m, 2H), 7.30 (m, 3H), 4.86–4.62 (m, 2H), 1.30 (d, *J*=6.2 Hz, 6H), 1.22 (d, *J*=6.2 Hz, 6H); $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ 134.2 (d, *J*=5.5 Hz), 129.2 (d, *J*=2.0 Hz), 128.6 (d, *J*=2.6 Hz), 127.3 (d, *J*=7.0 Hz), 73.3 (d, *J*=6.8 Hz), 23.8 (d, *J*=4.1 Hz), 23.5 (d, *J*=5.7 Hz); $^{31}P$ NMR ($CDCl_3$, 162 MHz): δ 20.4; IR (neat): 3476, 3061, 2981, 2934, 1958, 1882, 1725, 1632, 1581, 1474, 1386, 1329, 1254, 1145, 982, 747, 689, 596 $cm^{-1}$; HRMS (ESI-TOF) *m/z* calcd for $C_{12}H_{20}O_3PS$ $[M+H]^+$ 275.0871, found 275.0879.

*4.2.28. Thiophosphoric acid O,O′-diisobutyl ester S-phenyl ester (**5i**).* Colorless oil. Yield: 263 mg (87%). $^1H$ NMR ($CDCl_3$, 400 MHz): δ 7.56–7.53 (m, 2H), 7.36–7.27 (m, 3H), 3.91–3.78 (m, 4H), 1.96–1.82 (m, 2H), 0.87 (m, 12H); $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ 134.5 (d, *J*=5.3 Hz), 129.2 (d, *J*=2.1 Hz), 128.9 (d, *J*=2.8 Hz), 126.6 (d, *J*=7.0 Hz), 73.86 (d, *J*=7.2 Hz), 29.0 (d, *J*=7.4 Hz), 18.6; $^{31}P$ NMR ($CDCl_3$, 162 MHz): δ 22.7; IR (neat): 3492, 3061, 2962, 2875, 1630, 1582, 1471, 1395, 1255, 998, 863, 817, 747, 690, 604 $cm^{-1}$; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{24}O_3PS$ $[M+H]^+$ 303.1184, found 303.1188.

*4.2.29. Thiophosphoric acid O,O′-di-sec-butyl ester S-phenyl ester (**5j**).* Colorless oil. Yield: 169 mg (56%). $^1H$ NMR ($CDCl_3$, 400 MHz): δ 7.63–7.54 (m, 2H), 7.36–7.26 (m, 3H), 4.64–4.41 (m, 2H), 1.71–1.46 (m, 4H), 1.29–1.27 (m, 3H), 1.22–1.20 (m, 3H), 0.85 (m, 6H); $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ 134.2 (d, *J*=5.5 Hz), 129.1 (d, *J*=1.9 Hz), 128.6 (d, *J*=2.0 Hz), 127.4 (d, *J*=2.7 Hz), 30.2 (d, *J*=5.8 Hz), 21.0 (d, *J*=2.9 Hz), 20.7 (d, *J*=4.2 Hz), 9.3 (d, *J*=4.4 Hz); $^{31}P$ NMR ($CDCl_3$, 162 MHz): δ 20.8; IR (neat): 3488, 3061, 2974, 2880, 2740, 1958, 1724, 1631, 1463, 1381, 1256, 1125, 1027, 811, 697, 604 $cm^{-1}$; HRMS (ESI-TOF) *m/z* calcd for $C_{14}H_{24}O_3PS$ $[M+H]^+$ 303.1184, found 303.1188.

### 4.3. General procedure of the coupling between disulfides and diethyl phosphite (3a, 3e, 3p, 3r, 3u, 3v)

A Schlenk tube was charged with disulfide **4** (0.5 mmol), dialkyl phosphite **2** (2.0 mmol), and DTBP (2.0 mmol), then 1.5 mL DMSO was added as solvent. This reaction was performed under $N_2$ atmosphere at 80 °C for 20 h. After completion of the reaction, the mixture was quenched with 20 mL $Na_2S_2O_4$ solution (5%) then extracted with ethyl acetate (15 mL×3). The organic layer was combined and dried with anhydrous $Na_2SO_4$. After the evaporation in a vacuum, the crude product was purified by a gel column chromatography using petroleum ether/ethyl acetate as eluent to afford the desired product **3**.

*4.3.1. Thiophosphoric acid O,O′-diethyl ester S-p-tolyl ester (**3u**).* Colorless oil. Yield: 174.0 mg (67%). $^1H$ NMR ($CDCl_3$, 400 MHz): δ 7.42–7.40 (m, 2H), 7.13–7.11 (m, 2H), 4.21–4.08 (q, *J*=7.0 Hz, 4H), 2.31 (s, 3H), 1.29–1.26 (t, *J*=7.0 Hz, 6H); $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ 139.2 (d, *J*=3.1 Hz), 134.6 (d, *J*=5.1 Hz), 130.1 (d, *J*=2.3 Hz), 122.8 (d, *J*=7.3 Hz), 63.9 (d, *J*=6.2 Hz), 21.1, 16.0 (d, *J*=7.2 Hz); $^{31}P$ NMR ($CDCl_3$, 162 MHz): δ 23.3; IR (neat): 3491, 2983, 1492, 1443, 1391, 1254, 1161, 1014, 973, 810, 601 $cm^{-1}$; HRMS (ESI-TOF) *m/z* calcd for $C_{11}H_{18}O_3PS$ $[M+H]^+$ 261.0714, found 261.0708.

*4.3.2. Thiophosphoric acid O,O′-diethyl ester S-(2-nitro-phenyl) ester (**3v**).* Yellow oil. Yield: 78.7 mg (27%). $^1H$ NMR ($CDCl_3$, 400 MHz): δ 7.99–7.96 (m, 1H), 7.90–7.88 (m, 1H), 7.57–7.53 (m, 1H), 7.48–7.44 (m, 1H), 4.24–4.09 (m, 4H), 1.31–1.27 (m, 6H); $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ 151.7 (d, *J*=4.3 Hz), 136.1 (d, *J*=4.8 Hz), 132.8 (d, *J*=1.6 Hz), 129.2 (d, *J*=1.9 Hz), 125.2 (d, *J*=1.5 Hz), 123.1 (d, *J*=6.3 Hz), 64.9 (d, *J*=6.7 Hz), 16.0 (d, *J*=7.0 Hz); $^{31}P$ NMR ($CDCl_3$, 162 MHz): δ 19.9; IR (neat): 3489, 2986, 2908, 1529, 1355, 1258, 1162, 1012, 853, 782, 738, 651, 598 $cm^{-1}$; HRMS (ESI-TOF) *m/z* calcd for $C_{10}H_{15}NO_5PS$ $[M+H]^+$ 292.0409, found 292.0404.

### 4.4. TEMPO trapping experiment (6a)

A Schlenk tube was charged with disulfide **4** (0.5 mmol), dialkyl phosphite **2** (2.0 mmol), DTBP (2.0 mmol) and TEMPO (2.0 mmol), then 1.5 mL DMSO was added as solvent. This reaction was performed under $N_2$ atmosphere at 80 °C for 20 h. After completion of the reaction, the mixture was quenched with 20 mL $Na_2S_2O_4$ solution (5%) then extracted with ethyl acetate (15 mL×3). The organic layer was combined and dried with anhydrous $Na_2SO_4$. After the evaporation in a vacuum, the crude product was purified by a gel column chromatography using petroleum ether as eluent to afford the desired product **6a**.

*4.4.1. 2,2,6,6-Tetramethyl-1-(phenylthiooxy)piperidine (**6a**).* White solid, mp: 63–64 °C. Yield: 58 mg (22%). $^1H$ NMR ($CDCl_3$, 400 MHz): δ 7.70–7.63 (m, 2H), 7.46–7.39 (m, 2H), 7.39–7.33 (m, 1H), 1.82 (s, 1H), 1.62 (m, 5H), 1.49 (m, 8H), 1.35 (s, 1H), 0.88 (s, 3H); $^{13}C$ NMR ($CDCl_3$, 100 MHz): δ 150.4, 129.4, 128.7, 126.1, 77.5, 77.2, 76.9, 61.4, 59.0, 43.6, 41.5, 35.5, 32.7, 29.9, 17.4; IR (KBr): 3446, 2933, 1650, 1534, 1441, 1301, 1242, 1178, 1128, 1080, 1052, 908, 749, 698, 555, 453 $cm^{-1}$; HRMS (ESI-TOF) *m/z* calcd for $C_{15}H_{24}NOS$ $[M+H]^+$ 266.1579, found 266.1588.

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### Supplementary data

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