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Direct synthesis of thiophosphates by reaction of diphenylphosphine oxide with sulfonyl chlorides

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ABSTRACT

A new method for the synthesis of thiophosphates by reductive coupling reaction of diphenylphosphine oxide and sulfonyl chlorides has been developed. The reaction is metal-free and needs no additives, affording various aryl and alkyl substituted thiophosphates in good to excellent yields under mild conditions.

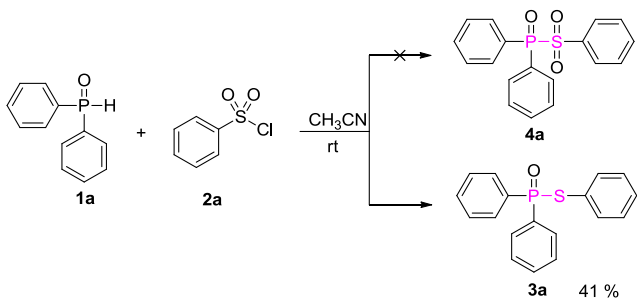
1. Introduction

Thiophosphate derivatives have attracted much attention in recent decades due to their widespread application in pharmaceuticals and agrochemicals.[1] Thus, many studies were carried out for the synthesis of thiophosphates. The reported methods for the synthesis of thiophosphates include Michaelis–Arbuzov reaction,[2] coupling reaction[3] and condensation reaction.[4] Traditional method for the synthesis of thiophosphates is via the nucleophilic substitution of phosphine chlorides with thiols. Recently, Wu and co-workers reported the copper-catalyzed reductive cross-coupling reaction of aryl sulfonyl chlorides with *H*-phosphonates.[5] Pan and co-workers discovered the reaction of H-phosphine oxide or *H*-phosphinate esters with thio/thiophenol using *tert*-butyl peroxybenzoate (TBPB) and KI as additives.[6] Although many efforts have been made to facilitate the synthesis of thiophosphates, some drawbacks still exist: needing fresh prepared raw materials,[7,8] using bases,[9–12] metal catalysts[13–16] or other additives.[17,18] Thus, the development of simple and environmental friendly synthesis methods remains unexplored.

2. Results and discussion

Herein, we wish to share our research about the direct synthesis of thiophosphates by the reaction of diphenylphosphine oxide/*H*-phosphinates/*H*-phosphonates with aryl/alkyl sulfonyl chlorides. Compared with the reported methods for the synthesis of thiophosphates, this reaction is metal-free and needs no additives to afford various substituted thiophosphates under mild conditions.

In the initial work, we attempted the reaction of diphenylphosphine oxide (**1a**) with benzenesulfonyl chloride (**2a**) for the synthesis of sulfonylphosphonate (**4a**) (Scheme 1). To our surprise, we obtained the deoxidized product *S*-phenyl diphenylphosphinothioate (**3a**) instead of **4a** by the MS analysis. To the best of our knowledge, the direct synthesis of thiosphonates by the reaction of diphenylphosphine oxide with sulfonyl chlorides in the absence of metal and additives has not been reported to date. The experiment results enlightened us to further examine the reaction between phosphine oxides and sulfonyl chlorides.



Scheme 1. Reductive coupling reaction of diphenylphosphine oxide with benzenesulfonyl chloride.

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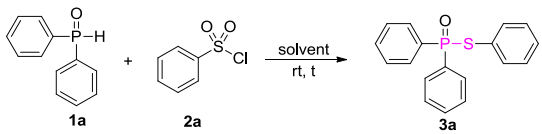
0040-4020/

With the consideration in mind, we attempted the reaction of diphenylphosphine oxide (**1a**) with benzenesulfonyl chloride (**2a**) under various conditions (Table 1). Firstly, the reaction was carried out in CH_3CN at room temperature. To our delight, the desired product (**3a**) was obtained in a yield of 41% within 5 h (Table 1, entry 1). We then prolonged the reaction time to 20 h, but the yield of **3a** was only increased by 10% (Table 1, entry 3). It was noted that a main byproduct diphenylphosphinic acid was also isolated, which consumed a portion of the reagent. Therefore, we investigated the effect of the reactant ratio between **1a** and **2a**. When the dosage of **1a** was increased to 2.5 equiv and 3 equiv, the product yields of **3a** were enhanced to 55% and 77%, respectively (Table 1, entries 4 and 5). Consequently, a fairly good yield (88%) of **3a** was obtained when the amount of **1a** was increased to 4 equiv (Table 1, entry 6). It should be noted that the byproduct diphenylphosphinic acid as a flame retardant was readily filtered for other applications. In addition, increasing the temperature from room temperature to 60 °C, the yield of **3a** was increased a bit: from 88 % to 92 % (Table 1, entry 7). Further increase the temperature resulted in no improvement of the yield. For comprehensive consideration, we performed the reaction at room temperature. After screening of the solvents including dichloromethane (DCM), dimethylformamide (DMF), dioxane and toluene, it was found that solvent had a little effect on the reaction (Table 1, entries 8–11) and CH_3CN was selected as the optimal solvent for this reaction.

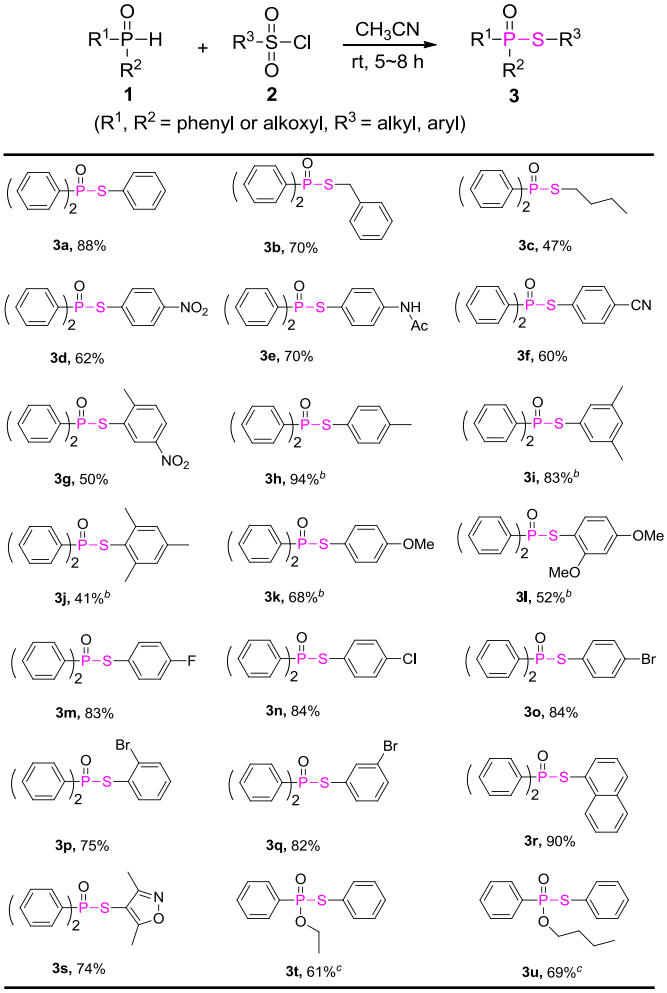
Table 1
Optimization of reaction conditions[a]



Entry	**1a**:**2a**	Solvent	*t* (h)	Yield (%)
1	2:1	CH_3CN	5	41
2	1.2:1	CH_3CN	20	25
3	2:1	CH_3CN	20	51
4	2.5:1	CH_3CN	20	55
5	3:1	CH_3CN	20	77
6	4:1	CH_3CN	5	88
7[b]	4:1	CH_3CN	3.5	92
8	4:1	DCM	5	81
9	4:1	DMF	5	86
10	4:1	Dioxane	5	82
11	4:1	Toluene	5	88

[a] Unless otherwise noted, the reactions were performed by adding **1a** and **2a** (1 mmol) in solvent (5 mL) at room temperature. Isolated yields.
[b] The reaction was performed at 60 °C.

Next, we investigated the scope and limitations of the reaction of diphenylphosphine oxide and *H*-phosphinates with aryl/alkyl sulfonyl chlorides under the optimized reaction conditions. As shown in Scheme 2, various aryl/alkyl sulfonyl chlorides could readily react with diphenylphosphine oxide to form thiophosphates in moderate to good yields. Comparing with the alkyl sulfonyl chloride, aryl sulfonyl chlorides was easier to react with diphenylphosphine oxide (Scheme 2, **3a**–**3c**). For the substrates of aryl sulfonyl chloride, the strong electron-withdrawing or -donating groups leaded to lower yields of the desired products (Scheme 2, **3d**–**3g** and **3k**–**3l**), while the weak electron-donating and -neutral groups resulted in good yields of thiophosphates (Scheme 2, **3h, 3r**). The steric hindrance also affected the reaction between diphenylphosphine oxide and aryl sulfonyl chlorides. Although the bromine substituted (o-, m-, p-) phenylsulfonyl chloride showed little effect on the reaction (Scheme 2, **3o**–**3q**), the employment of 2,4,6-trimethylbenzensulfonyl chloride gave a much lower yield (Scheme 2, **3j**). In addition, heteroaromatic sulfonyl chloride could also react with diphenylphosphine oxide, affording the product in moderate yield under the standard conditions (Scheme 2, **3s**). Moreover, the reaction of *H*-phosphinates with aryl sulfonyl chlorides proceeded smoothly at 80 °C to give the thiophosphate derivatives in moderate yields (Scheme 2, **3t**–**3u**).



[a]Unless otherwise noted, the reactions were performed by adding diphenyl phosphine oxide or *H*-phosphinates (4 mmol), sulfonyl chlorides (1 mmol) and CH_3CN (5 ml) at room temperature for 5 h. Isolated yields.
[b]Reactions were performed for 8 h.
[c]Reactions were performed at 80 °C for 9 h.

Scheme 2. Reaction of diphenylphosphine oxide/*H*-phosphinates with sulfonyl chlorides.[a]

With the excited and promising results in hand, we envisioned that the reaction of *H*-phosphonates and aryl sulfonyl chlorides could also provide the thiophosphate derivatives (Scheme 3). However, it was found that the reaction between *H*-phosphonate and aryl sulfonyl chlorides showed low efficiency. Although the reaction temperature was increased to 150 °C, the yields of the desired products were still lower (Scheme 3, **3v**–**3w**). The results indicated that the reaction activity towards aryl sulfonyl chlorides under the standard conditions is as follows: diphenylphosphine oxide>*H*-phosphinates>*H*-phosphonates.

It is also possible to prepare thiophosphates on a gram scale. As shown in Scheme 4, a good yield was provided for the gram-scale synthesis of **3a**, thus offering a reliable and practical access to the synthesis of thiophosphates under mild conditions.

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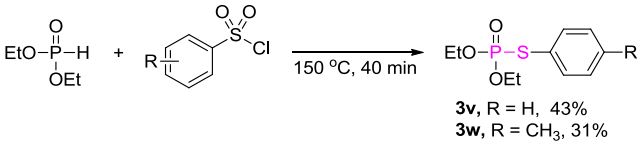
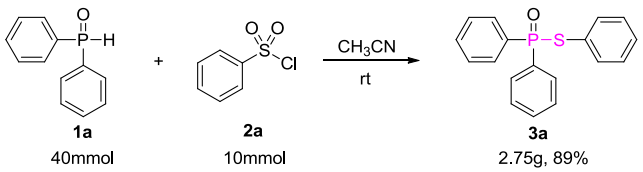
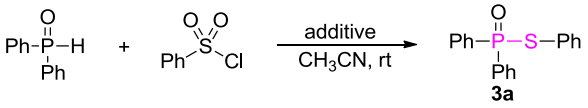


Scheme 3. Reactions of *H*-phosphonate with sulfonyl chlorides.



Scheme 4. Gram-Scale synthesis of thiophosphate.

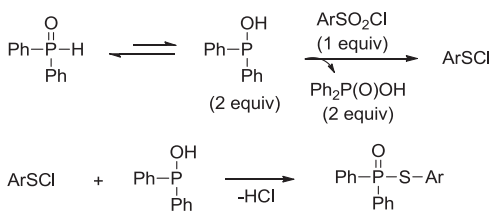
To gain the mechanism insights into the present reaction, we performed the reaction of diphenylphosphine oxide (**1a**) with benzenesulfonyl chloride (**2a**) in the presence of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as a radical inhibitor and hydroquinone as an inhibitor of SET steps (Scheme 5). No significant decrease of the reaction efficiency was observed. And the results indicated that the reaction was impossible to proceed through a radical pathway.



additive	**3a**, yield (%)
no	88
TEMPO (2.0 equiv)	47
hydroquinone (2.0 equiv)	61

Scheme 5. Radical inhibition experiments.

According to the previous reports[2,19] and our experiment results, a plausible reaction mechanism of the reaction between diphenylphosphine oxide and aryl sulfonyl chlorides was proposed (Scheme 6). The diphenylphosphine oxide firstly tautomerized to diphenylphosphinous acid, and then involved in sequential deoxygenation of sulfonyl chlorides to form sulfinyl chloride (confirmed by MS in this work).[2,8b,18] Then the intermediate of sulfinyl chloride reacted with diphenylphosphinous acid to afford the product *S*-phenyl diphenylphosphinothioates.



Scheme 6. Proposed reaction mechanism.

3. Conclusions

In conclusion, we have discovered a new method for the synthesis of thiophosphates by the reaction of diphenylphosphine oxide/*H*-phosphinates/*H*-phosphonates with aryl/alkyl sulfonyl chlorides. This synthesis method is metal-free and need of no additives, offering a practical access to the synthesis of thiophosphates under mild conditions. A plausible mechanism was proposed.

4. Experimental section

4.1. General information

Reagents and solvents were purchased from commercial suppliers and used without additional purification. ^{1}H NMR, ^{31}P NMR and ^{13}C NMR spectra were recorded on a BrukerARX-400. FTIR spectra were obtained with a Nicolet 380 spectrophotometer. Mass spectra were obtained on an Agilent LC-MS 1100 instrument. High resolution mass data were recorded on a Thermo Fisher Scientific LTQ FT Ultra instrument. Elemental analysis was performed with Elementer Vario EL III instrument. Melting points were recorded on a SGW X-4 melting point apparatus and the thermometer is uncorrected.

4.2. General procedure for the preparation of products (3a–3s)

Sulfonyl chlorides (1.0 mmol) and diphenylphosphine oxide (4.0 mmol) were dissolved in 5 mL CH_3CN in a round-bottom flask and reacted at room temperature for 5 h. After reaction completion, diphenylphosphinic acid was filtered off, the solid was washed with CH_3CN (2×5 mL). Then the filtrate was evaporated under vacuum. The crude product was purified by silica gel column chromatography using petroleum ether-EtOAc (3:1) as the eluent.

*4.2.1. S-phenyl diphenylphosphinothioate (**3a**).* White solid (271 mg, 88%). Mp: 84–86 °C. IR (KBr):1203, 1108, 746, 560 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85(dd, J_1=13.2 Hz, J_2=8.0 Hz, 4H), 7.53–7.49 (m, 2H), 7.46–7.42 (m, 6H), 7.26–7.18(m. 3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 41.3 (s, 1P). ^{13}C NMR (100 MHz, $CDCl_3$): δ 126.3(d, J=5.1 Hz), 128.5(d, J=13.1 Hz), 128.9(d, J=1.4 Hz), 129.1(d, J=1.4 Hz), 131.6(d, J=10.2 Hz), 132.3(d, J=2.9 Hz), 132.6(d, J=106.5 Hz), 135.4(d, J=3.6 Hz). MS (ESI, m/z): 311.0 (M+H)$^{+}$. Anal. Calcd. For $C_{18}H_{15}OPS$(%): C, 69.66; H, 4.87. Found: C, 69.95; H, 5.01.

*4.2.2. S-benzyl diphenylphosphinothioate (**3b**).* White solid (224 mg, 70%). Mp: 92–94 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90–7.84 (m, 4H), 7.54–7.50 (m, 2H), 7.47–7.42 (m, 4H), 7.22–7.15 (m, 5H), 4.03 (d, J=8.8 Hz, 2H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 42.7 (s, 1P). ^{13}C NMR (100 MHz, $CDCl_3$): δ 33.2 (d, J=2.2 Hz), 127.5, 128.6 (d, J=2.9 Hz), 128.8, 129.0, 131.5(d, J=10.2 Hz), 132.4(d, J=3.6 Hz), 133.1(d, J=106.4 Hz), 136.8(d, J=5.1 Hz).

*4.2.3. S-butyl diphenylphosphinothioate (**3c**).* Colorless oil (137 mg, 47%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92–7.86 (m, 4H), 7.54–7.49 (m, 2H), 7.48–7.44 (m, 4H), 2.83–2.77 (m, 2H), 1.64–1.56 (m, 2H), 1.29–1.24 (m, 2H), 0.74 (t, J=6.8 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 42.9 (s, 1P). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.4, 21.7, 29.0(d, J=2.2 Hz), 32.6(d, J=5.1 Hz), 128.6(d, J=13.2 Hz), 131.4(d, J=10.3 Hz), 132.2(d, J=3.0 Hz), 133.5(d, J=106.5 Hz).

*4.2.4. S-(4-nitrophenyl) diphenylphosphinothioate (**3d**).* Yellow solid (220 mg, 62%). Mp: 105–107 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J=8.8 Hz, 2H), 7.86(dd, J_1=12.8 Hz, J_2=6.8 Hz, 4H), 7.68 (d, J=8.4 Hz, 2H), 7.58–7.54 (m, 2H), 7.50–7.46 (m, 4H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 41.9 (s, 1P). ^{13}C NMR (100 MHz, $CDCl_3$): δ 123.9, 128.9(d, J=13.2 Hz), 131.6(d, J=10.9 Hz), 131.8(d, J=107.2 Hz), 132.9(d, J=2.9 Hz), 135.1(d, J=4.4 Hz), 136.1(d, J=4.4 Hz), 147.9(d, J=2.2 Hz).

*4.2.5. S-(4-acetamidophenyl) diphenylphosphinothioate (**3e**).* White solid (255 mg, 70%). Mp: 146–147 °C. ^{1}H NMR (400 MHz, $CDCl_3$):

δ 9.66 (br, 1H), 7.86–7.81 (m, 4H), 7.56–7.54 (m, 2H), 7.50–7.43 (m, 6H), 7.22 (d, *J*=8.4 Hz, 2H), 2.1 (s, 3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 42.6 (s, 1P). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.5, 118.1 (d, *J*=5.8 Hz), 120.3, 128.8(d, *J*=13.1 Hz), 131.5(d, *J*=10.2 Hz), 132.2(d, *J*=106.4 Hz), 132.6(d, *J*=2.1 Hz), 136.4(d, *J*=2.9 Hz), 140.4, 169.4.

*4.2.6. S-(4-cyanophenyl) diphenylphosphinothioate (**3f**).* White solid (202 mg, 60%). Mp:107–109 °C. IR (KBr): 2232, 1215, 1102, 755, 551 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88–7.83 (m, 4H), 7.63–7.61 (m, 2H), 7.58–7.54 (m, 2H), 7.51–7.46 (m, 6H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 41.8 (s, 1P). ^{13}C NMR (100 MHz, $CDCl_3$): δ 112.5 (d, *J*=1.4 Hz), 118.1, 128.9(d, *J*=6.9 Hz), 131.6(d, *J*=10.2 Hz), 131.8(d, *J*=107.9 Hz), 132.4(br), 132.8(d, *J*=2.9 Hz), 133.8(d, *J*=5.1 Hz), 135.2(d, *J*=4.4 Hz).MS (ESI, *m*/*z*): 336.0 $(M+H)^+$. Anal. Calcd. For $C_{19}H_{14}NOPS$(%): C, 68.05; H, 4.21; N, 4.18. Found: C, 68.22; H, 4.14; N, 4.04.

*4.2.7. S-(2-methyl-5-nitrophenyl) diphenylphosphinothioate (**3g**).* Light yellow solid (182 mg, 50%). Mp: 91–94 °C. IR (KBr):1508, 1434, 1204, 1113, 758, 554 cm^{-1}. ^{1}H NMR (400 MHz, CDCl3): δ 8.11 (s, 1H), 8.00 (d, *J*=8.8 Hz, 1H), 7.86(dd, J_1=12.8 Hz, J_2=7.2 Hz, 4H), 7.58–7.54 (m, 2H), 7.51–7.46 (m, 4H), 7.34 (d, *J*=8.4 Hz, 1H), 2.57 (s, 3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 42.0 (s, 1P). ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.0, 123.9(d, *J*=2.2 Hz), 127.8(d, *J*=5.8 Hz), 128.8(d, *J*=13.8 Hz), 131.2(d, *J*=1.5 Hz), 131.4(d, *J*=4.4 Hz), 131.5(d, *J*=10.2 Hz), 131.9(d, *J*=105.8 Hz), 132.9(d, *J*=3.0 Hz), 145.9(d, *J*=1.5 Hz), 151.4(d, *J*=2.9 Hz).MS (ESI, *m*/*z*):370.0 $(M+H)^+$. Anal. Calcd. For $C_{19}H_{16}NO_3PS$(%): C, 61.78; H, 4.37; N, 3.79. Found: C, 62.04; H, 4.30; N, 3.61.

*4.2.8. S-(4-methylphenyl) diphenylphosphinothioate (**3h**).* White solid (235 mg, 94%). Mp: 106–107 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85(dd, J_1=13.2 Hz, J_2=7.2 Hz, 4H), 7.51–7.49 (m, 2H), 7.44–7.40 (m, 4H), 7.32(d. *J*=6.8 Hz, 2H), 6.99(d, 7.6 Hz, 2H), 2.23 (s, 3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 41.2 (s, 1P). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2, 122.3(d, *J*=5.1 Hz), 128.5(d, *J*=13.1 Hz), 130.0(d, *J*=1.4 Hz), 131.7(d, *J*=10.2 Hz), 132.3(d, *J*=2.9 Hz), 132.7(d, *J*=105.8 Hz), 135.4(d, *J*=3.6 Hz), 139.2(d, *J*=2.9 Hz). MS (ESI, *m*/*z*): 324.9 $(M+H)^+$.

*4.2.9. S-(3,5-dimethylphenyl) diphenylphosphinothioate (**3i**).* White solid (280 mg, 83%). Mp: 112–113 °C. IR (KBr):1439, 1204, 1102, 755, 566 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88–7.83 (m, 4H), 7.52–7.49 (m, 2H), 7.46–7.43 (m, 4H), 7.03 (s, 2H), 6.86 (s, 1H), 2.16 (s, 6H). ^{31}P NMR (162 MHz, CDCl3): δ 41.1 (s, 1P). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 125.3(d, *J*=5.1 Hz), 128.5(d, *J*=13.1 Hz), 130.8(d, *J*=2.2 Hz), 131.7(d, *J*=10.2 Hz), 132.2(d, *J*=3.0 Hz), 132.8(d, *J*=105.7 Hz), 133.1(d, *J*=4.4 Hz), 138.7(d, *J*=2.2 Hz).MS (ESI, *m*/*z*): 339.1 $(M+H)^+$. Anal. Calcd. For $C_{20}H_{19}OPS$(%): C, 70.98; H, 5.66. Found: C, 71.21; H, 5.62.

*4.2.10. S-(2,4,6-thimethylphenyl) diphenylphosphinothioate (**3j**).* White solid (124 mg, 41%). Mp: 95–96 °C. IR (KBr): 1437, 1193, 1112, 723, 567 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79–7.74 (m, 4H), 7.54–7.50 (m, 2H), 7.44–7.39 (m, 4H), 6.84 (s, 2H), 2.24 (s, 6H), 2.23 (s, 3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ39.4 (s, 1P). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.0, 22.4, 120.8(d, *J*=6.6 Hz), 128.4(d, *J*=13.1 Hz), 129.4(d, *J*=2.2 Hz), 131.4(d, *J*=10.2 Hz), 132.2(d, *J*=2.9 Hz), 133.5(d, *J*=105.0 Hz), 139.3(d, *J*=2.9 Hz), 144.8(d, *J*=3.6 Hz).MS (ESI, *m*/*z*): 353 $(M+H)^+$. HRMS (ESI): calcd. For $C_{21}H_{21}OPS$ $(M+H)^+$: 353.1119, found: 353.1123.

*4.2.11. S-(4-methoxyphenyl) diphenylphosphinothioate (**3k**).* White solid (230 mg, 68%). Mp: 131–134 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87–7.81 (m, 4H), 7.53–7.49 (m, 2H), 7.46–7.41 (m, 4H),7.34–7.32 (m, 2H), 6.73 (d, *J*=9.2 Hz, 2H), 3.73 (s, 3H). ^{31}P NMR (162 MHz, CDCl3): δ 41.2 (s, 1P). ^{13}C NMR (100 MHz, $CDCl_3$): δ55.3, 114.8(d, *J*=1.4 Hz), 116.1(d, *J*=5.1 Hz), 128.5(d, *J*=13.2 Hz), 131.7(d, *J*=10.3 Hz), 132.2(d, *J*=2.9 Hz), 132.7(d, *J*=102.1 Hz), 137.1(d, *J*=3.6 Hz), 160.5(d, *J*=2.2 Hz).

*4.2.12. S-(2,4-dimethoxyphenyl) diphenylphosphinothioate (**3l**).* Colorless oil (153 mg, 52%). IR (KBr): 2354, 1210, 1114, 742, 555 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89–7.84 (m, 4H), 7.58(dd, J_1=8.8 Hz, J_2=1.6 Hz, 1H), 7.49–7.45 (m, 2H), 7.42–7.37 (m, 4H), 6.42(dd, J_1=8.8 Hz, J_2=2.8 Hz, 1H), 6.25 (d, *J*=2.4 Hz, 1H), 3.72 (s, 3H), 3.50 (s, 3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 41.3 (s, 1P). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.40, 55.43, 99.1(d, *J*=2.2 Hz), 104.2(d, *J*=5.8 Hz), 105.4, 128.2(d, *J*=13.2 Hz), 131.6(d, *J*=10.9 Hz), 132.1(d, *J*=2.9 Hz), 133.2(d, *J*=105.0 Hz), 139.0(d, *J*=3.7 Hz), 160.7(d, *J*=2.9 Hz), 162.3(d, *J*=1.4 Hz).MS (ESI, *m*/*z*): 371.1 $(M+H)^+$. HRMS (ESI): calcd. For $C_{20}H_{19}O_3PS$ $(M+H)^+$: 371.0862, found: 371.0865.

*4.2.13. S-(4-fluorophenyl) diphenylphosphinothioate (**3m**).* White solid (272 mg, 83%). Mp: 94–96 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85(dd, J_1=13.2 Hz, J_2=7.6 Hz, 4H), 7.52–7.48 (m, 2H), 7.45–7.43 (m, 6H), 6.89 (t, *J*=8.0 Hz, 2H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 41.4 (d, *J*=3.9 Hz, 1P). ^{19}F NMR (376 MHz, $CDCl_3$): δ −111.6 (d, *J*=5.6 Hz, 1F). ^{13}C NMR (100 MHz, $CDCl_3$): δ 116.3(dd, J_1=21.9 Hz, J_2=1.4 Hz), 121.2(t, *J*=4.3 Hz), 128.6(d, *J*=13.2 Hz), 131.6(d, *J*=10.2 Hz), 132.3(d, *J*=106.4 Hz), 132.5(d, *J*=3.0 Hz), 137.4(dd, J_1=8.8 Hz, J_2=3.7 Hz), 163.4(dd, J_1=248.7 Hz, J_2=2.2 Hz).

*4.2.14. S-(4-chlorophenyl) diphenylphosphinothioate (**3n**).* White solid (293 mg, 84%). Mp: 104–105 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87–7.81 (m, 4H), 7.55–7.51 (m, 2H), 7.48–7.43 (m, 4H), 7.39–7.37 (m, 2H), 7.17 (d, *J*=8.4 Hz, 2H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 41.4 (s, 1P). ^{13}C NMR (100 MHz, $CDCl_3$): δ 124.8(d, *J*=5.1 Hz), 128.7(d, *J*=13.1 Hz), 129.3(d, *J*=1.4 Hz), 131.6(d, *J*=10.2 Hz), 132.3(d, *J*=106.5 Hz), 132.5(d, *J*=2.9 Hz), 135.5(d, *J*=2.2 Hz), 136.5(d, *J*=3.6 Hz).

*4.2.15. S-(4-bromophenyl) diphenylphosphinothioate (**3o**).* White solid (328 mg, 84%). Mp: 102–103 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87–7.82 (m, 4H), 7.51–7.48 (m, 2H), 7.45–7.40 (m, 4H), 7.33–7.29 (m, 4H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 41.3 (s, 1P). ^{13}C NMR (100 MHz, $CDCl_3$): δ 123.8(d, *J*=2.9 Hz), 125.5(d, *J*=5.1 Hz), 128.7(d, *J*=13.1 Hz), 131.6(d, *J*=10.2 Hz), 132.2(d, *J*=106.4 Hz), 132.3(d, *J*=2.2 Hz), 132.6(d, *J*=2.9 Hz), 136.8(d, *J*=3.7 Hz).

*4.2.16. S-(2-bromophenyl) diphenylphosphinothioate (**3p**).* White solid (292 mg, 75%). Mp:76–78 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94–7.85 (m, 5H), 7.52–7.48 (m, 2H), 7.46–7.41 (m, 5H), 7.18(td, J_1=8.0 Hz, J_2=1.2 Hz, 1H), 7.07–7.03 (m, 1H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 42.2 (s, 1P). ^{13}C NMR (100 MHz, $CDCl_3$): δ 127.9, 128.3(d, *J*=5.1 Hz), 128.6(d, *J*=13.2 Hz), 129.0(d, *J*=4.4 Hz), 130.0, 131.7(d, *J*=10.2 Hz), 132.2(d, *J*=107.2 Hz), 132.6(d, *J*=2.9 Hz), 133.4, 136.5 (d, *J*=4.4 Hz).

*4.2.17. S-(3-bromophenyl) diphenylphosphinothioate (**3q**).* White solid (319 mg, 82%). Mp: 93–95 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85(dd, J_1=13.2 Hz, J_2=7.2 Hz, 4H), 7.55–7.41 (m, 8H), 7.34 (d, *J*=8.0 Hz, 1H), 7.03 (t, *J*=7.6 Hz, 1H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 41.5 (s, 1P). ^{13}C NMR (100 MHz, $CDCl_3$): δ 122.5(d, *J*=2.2 Hz), 128.4(d, *J*=5.1 Hz), 128.7(d, *J*=13.1 Hz), 130.3(d, *J*=1.4 Hz), 131.6(d, *J*=10.2 Hz), 132.1(d, *J*=106.5 Hz), 132.1(d, *J*=2.1 Hz), 132.6(d, *J*=3.7 Hz), 133.9(d, *J*=4.4 Hz), 137.6(d, *J*=3.6 Hz).

*4.2.18. S-naphthalen-1-yl diphenylphosphinothioate (**3r**).* White solid (323 mg, 90%). Mp: 106–107 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (d, *J*=8.4 Hz, 1H), 7.85–7.80 (m, 5H), 7.71 (t, *J*=7.6 Hz, 2H), 7.47–7.38 (m, 4H), 7.34–7.25 (m, 5H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 41.4 (s, 1P). ^{13}C NMR (100 MHz, $CDCl_3$): δ 123.7(d, *J*=5.9 Hz), 125.6(d, *J*=2.2 Hz), 126.0, 126.2, 126.8, 128.3, 128.5(d, *J*=13.1 Hz),

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130.0(d, J=2.2 Hz), 131.5(d, J=10.2 Hz), 132.3(d, J=2.9 Hz), 132.5(d, J=106.5 Hz), 134.1, 135.0(d, J=2.9 Hz), 135.6(d, J=4.4 Hz).

*4.2.19. S-(3,5-dimethylisoxazol-4-yl) diphenylphosphinothioate (**3s**).* White solid (243 mg, 74%). Mp: 108–110 °C. IR (KBr): 1586, 1434, 1189, 1121, 751, 551 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.86–7.81 (m, 4H), 7.61–757 (m, 2H), 7.53–7.49 (m, 4H), 2.18 (d, J=4.0 Hz, 3H), 2.05 (s, 3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 41.6 (s, 1P). ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.1, 11.5, 97.4(d, J=5.1 Hz), 128.8(d, J=13.1 Hz), 131.4(d, J=10.2 Hz), 132.1(d, J=104.3 Hz), 132.8(d, J=3.7 Hz), 162.7, 174.7 (d, J=4.4 Hz).MS (ESI, m/z):330.0 $(M+H)^+$. Anal. Calcd. For $C_{17}H_{16}NO_2PS$(%): C, 61.99; H, 4.90; N, 4.25. Found: C, 62.23; H, 4.74; N, 4.09.

4.3. General procedure for the preparation of products (3t, 3u)

Sulfonyl chlorides (1.0 mmol) and *H*-phosphinates (4.0 mmol) were dissolved in 5 mL CH_3CN in a round-bottom flask and reacted at 80 °C for 9 h. After reaction completion, the mixture was evaporated under vacuum. The crude product was purified by silica gel column chromatography using PE-EtOAc (3:1) as the eluent.

*4.3.1. O-ethyl S-phenyl phenylphosphonothioate (**3t**).* Yellow oil (156 mg, 61%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.66(dd, J_1=13.6 Hz, J_2=8.0 Hz, 2H), 7.50 (t, J=7.2 Hz, 1H), 7.40–7.35 (m, 2H), 7.32–7.27 (m, 3H), 7.21 (t, J=7.6 Hz, 2H), 4.41–4.31 (m, 2H), 1.41 (t, J=6.8 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ41.7 (s, 1P). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.3(d, J=6.5 Hz), 62.5(d, J=6.5 Hz), 126.6(d, J=5.1 Hz), 128.2(d, J=14.6 Hz), 129.0(d, J=2.9 Hz), 129.1(d, J=2.2 Hz), 131.47(d, J=10.2 Hz), 131.54(d, J=150.2 Hz), 132.5(d, J=3.0 Hz), 135.5(d, J=4.3 Hz).

*4.3.2. O-butyl S-phenyl phenylphosphonothioate (**3u**).* Yellow oil (213 mg, 69%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.67–7.62 (m, 2H), 7.51–7.49 (m, 1H), 7.39–7.34 (m, 2H), 7.31–7.26 (m, 3H), 7.20 (t, J=7.2 Hz, 2H), 4.35–4.22 (m, 2H), 1.77–1.70 (m, 2H), 1.48–1.39 (m, 2H), 0.94 (t, J=7.6 Hz, 3H). ^{31}P NMR (162 MHz, $CDCl_3$): δ 41.5 (s, 1P). ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.6, 18.8, 32.4(d, J=6.5 Hz), 66.1(d, J=7.3 Hz), 126.7(d, J=5.1 Hz), 128.2(d, J=15.3 Hz), 128.9(d, J=2.9 Hz), 129.1(d, J=2.2 Hz), 131.4(d, J=10.2 Hz), 131.6(d, J=149.5 Hz), 132.5(d, J=2.9 Hz), 135.5(d, J=4.4 Hz).

4.4. General procedure for the preparation of products (3v, 3w)

Sulfonyl chlorides (1.0 mmol) and *H*-phosphonate esters (4.0 mmol) were added in a round-bottom flask and reacted at 150 °C for 40 min. After reaction completion, the crude product was purified by silica gel column chromatography using PE-EtOAc (3:1) as the eluent.

*4.4.1. O,O-diethyl S-phenyl phosphorothioate (**3v**).* Light yellow oil (105 mg, 43%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.59–7.56 (m, 2H), 7.37–7.35 (m, 3H), 4.27–4.11 (m, 4H), 1.33–1.29 (m, 6H). ^{31}P NMR (162 MHz, $CDCl_3$): δ22.8 (s, 1P). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.0(d, J=7.3 Hz), 64.1(d, J=5.8 Hz), 126.6(d, J=7.3 Hz), 129.0(d, J=2.9 Hz), 129.4(d, J=2.2 Hz), 134.6(d, J=5.1 Hz).

*4.4.2. O,O-diethyl S-p-tolyl phosphorothioate (**3w**).* Light yellow oil (75 mg, 31%). ^1H NMR (400 MHz, $CDCl_3$): δ7.44(dd, J_1=8.0 Hz, J_2=1.6 Hz, 2H), 7.16 (d, J=8.0 Hz, 2H), 4.26–4.11 (m, 4H), 2.34 (s, 3H), 1.33–1.29(td, J_1=6.8 Hz, J_2=0.8 Hz, 6H). ^{31}P NMR (162 MHz, $CDCl_3$): δ23.8 (s, 1P). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.0 (d, J=7.3 Hz), 21.2, 64.0(d, J=6.6 Hz), 122.8(d, J=7.3 Hz), 130.2(d, J=2.2 Hz), 134.6(d, J=5.1 Hz), 139.3(d, J=2.9 Hz).

Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2016.10.012.

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