Synthesis N. K. Gusarova et al. Paper

Catalyst- and Solvent-Free Rapid Addition of Secondary Phosphine Chalcogenides to Aldehydes: Another Click Chemistry

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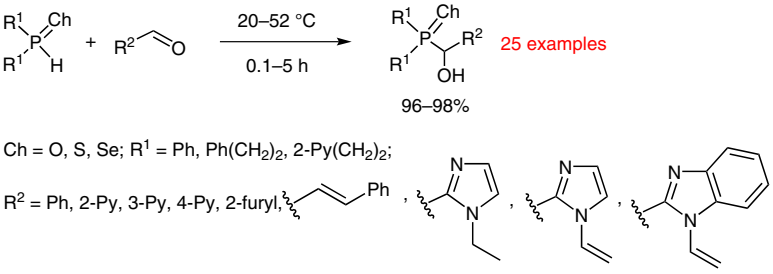

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Abstract An efficient catalyst- and solvent-free method for the synthesis of tertiary α-hydroxyphosphine chalcogenides, via the almost quantitative addition of secondary phosphine chalcogenides to diverse aldehydes under mild conditions (20–52 °C, from 10 min to 5 h), is reported.

Key words addition, aldehydes, green method, phosphine chalcogenides

Addition reactions remain among the most important approaches to atom-economic syntheses of diverse organic and elementoorganic compounds. Particular emphasis is placed on green click methods, which are implemented under mild conditions using available starting materials and reagents without catalyst and solvent with a minimum number of reaction steps, and efficient strategies for product isolation and purification to ensure high yields of adducts.

Over the last decade, important examples of hydrophosphorylation of aldehydes with secondary phosphine oxides,[1] sulfides,[1k,2] and selenides[1k,2c,3] have been reported. Addition of these P–H compounds across the C=O bonds proceeds in the harmful organic solvents such as tetrahydrofuran,[1d,e,g,m,2a] 1,4-dioxane,[1b,c] methanol,[1a] benzene,[1k] and dichloromethane[1f,l] at 20–52 °C or in the presence of sodium carbonate under microwave activation (110 °C, 20 min)[1j] to afford tertiary α-hydroxyphosphine chalcogenides. The latter can be used as ligands for the design of metal complex catalysts,[4] flame retardants for polymeric materials,[5] reagents for pulp bleach,[6] as well as drug precursors[7] with, for example, antiviral properties.[7b]

Here we report an improved green route toward α-hydroxyphosphine chalcogenides via addition of available secondary phosphine chalcogenides (easily prepared from aryl or hetaryl ethenes, elemental phosphorus, sulfur, or selenium[8]) to diverse aldehydes under catalyst- and solvent-free conditions.

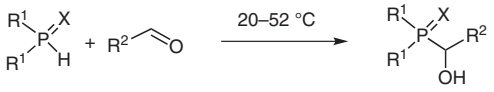
Based on the examples of bis(2-phenylethyl)phoshine oxide (**1**), diphenylphosphine oxide (**2**) and bis(2-phenylethyl)phoshine sulfide (**3**), we have shown that secondary phosphine oxides and sulfides react with aldehydes **4**–**11** under mild conditions (r.t. or 50–52 °C, from 10 min to 3 h, no catalyst and solvent) to give the corresponding tertiary α-hydroxyphosphine oxides **12a**–**k** and sulfide **12l** in almost quantitative yields (Table 1).

Previously, it has been shown that implementation of the above reactions in the presence of organic solvents (THF, benzene, CH_2Cl_2, 1,4-dioxane), with other conditions being the same, requires a longer reaction time (up to 84 times) (Table 1). The other benefit of the solvent-free reactions includes higher (in some cases) yield of the end products **12a**–**l** (Table 1, entries 1, 2, 7, 8, 12).

This green solvent-free protocol is successfully expanded by us over secondary phosphine sulfides **3**, **13**, **14** and selenides **15**, **16** as well as over other aldehyde **17**. Thus, a series of previously unknown tertiary α-hydroxyphosphine chalcogenides **18a**–**m** have been prepared in 96–98% yields (Table 2).

In the ^{1}H NMR spectra of the compounds **12** and **18**, the most typical signals are those of the HOCHP=X (O, S, Se) group. These signals are observed as a doublet at 4.4–6.3 ppm, with the coupling constants ^{31}P–C–^{1}H of 1.8–11.9 Hz. Noteworthy, the geminal constants ^{31}P–C–^{1}H in spectra of some α-hydroxyphosphine chalcogenides are small thus making the splitting of proton resonance signal not always observable.[3,9] As a result, the signals of tertiary phosphine chalcogenides may show up as a singlet. In the ^{13}C NMR spectra of the compounds **12** and **18**, the signals of HOCHP=X fragments appear as a typical doublet at ~63.1–73.5 ppm with the ^{31}P–^{13}C constant being equal to 42.7–87.5 Hz.

Table 1 Solvent-Free Synthesis of Tertiary α-Hydroxyphosphine Chalcogenides **12a–l** and Known Data for Similar Synthesis in a Solvent[a,b]



1–3 **4–11** **12a–l**

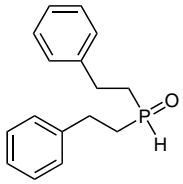
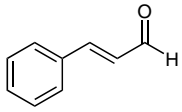
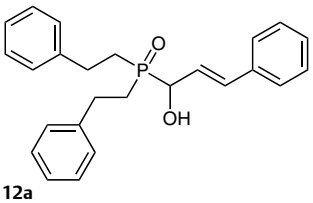
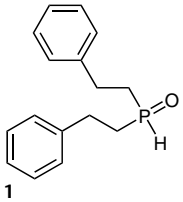
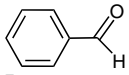
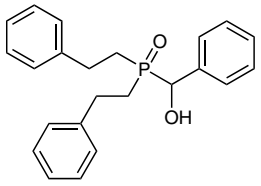
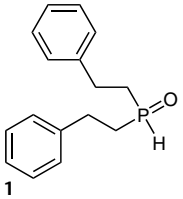
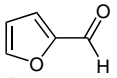
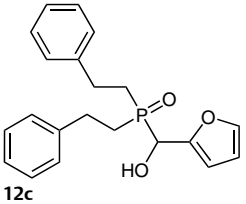
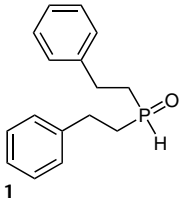
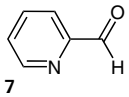
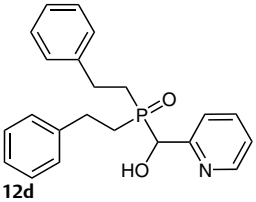
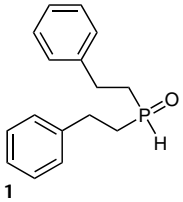
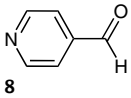
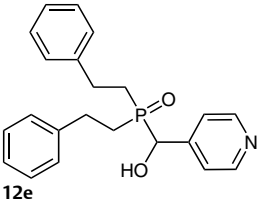
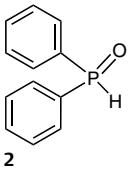
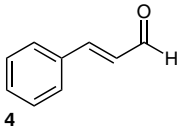
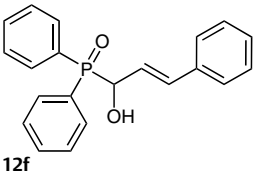
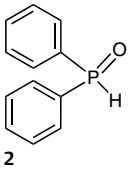
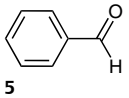
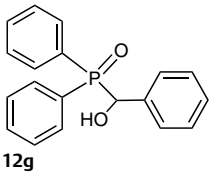
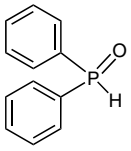
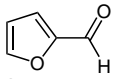
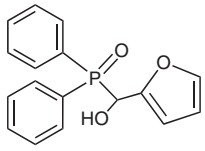
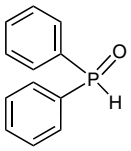
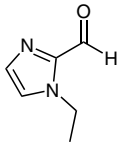
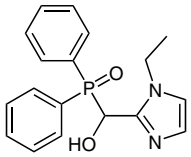
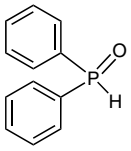
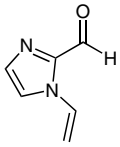
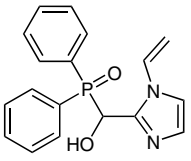
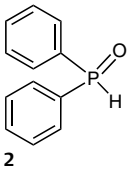
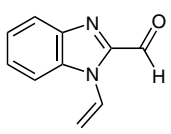
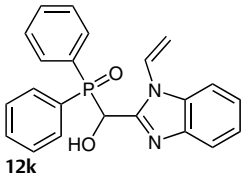
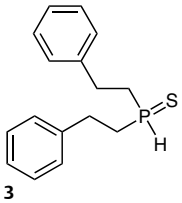
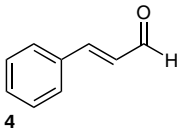
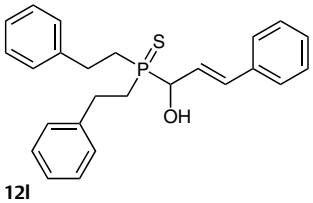
Entry	Phosphine chalcogenide	Aldehyde	Temp (°C)	Reaction time[b]	Product **12**	Isolated yield (%)[b]
1	 **1**	 **4**	20–22	3 h (84 h)[1d]	 **12a**	96 (87)[1d]
2	 **1**	 **5**	50–52	2 h (10 h)[1c]	 **12b**	97 (82)[1c]
3	 **1**	 **6**	50–52	1 h (26 h)[1e]	 **12c**	98 (98)[1e]
4	 **1**	 **7**	20–22	15 min (1.5 h)[1k]	 **12d**	98 (99)[1k]
5	 **1**	 **8**	20–22	30 min (2 h)[1k]	 **12e**	97 (92)[1k]
6	 **2**	 **4**	20–22	30 min (24 h)[1l]	 **12f**	97 (99)[1l]
7	 **2**	 **5**	20–22	15 min (50 min)[1m]	 **12g**	98 (85)[1m]

Table 1 (continued)

Entry	Phosphine chalcogenide	Aldehyde	Temp (°C)	Reaction time[b]	Product **12**	Isolated yield (%)[b]
8	 **2**	 **6**	20–22	30 min (24 h)[1f]	 **12h**	98 (77)[1f]
9	 **2**	 **9**	20–22	10 min (1 h)[1b]	 **12i**	97 (99)[1b]
10	 **2**	 **10**	20–22	30 min (1 h)[1b]	 **12j**	96 (96)[1b]
11	 **2**	 **11**	20–22	45 min (1 h)[1b]	 **12k**	97 (97)[1b]
12	 **3**	 **4**	50–52	3 h (40 h)[2a]	 **12l**	96 (75)[2a]

[a] Standard reaction conditions: molar ratio phosphine chalcogenides **1**–**3**/aldehydes **4**–**11** = 1:1, argon.
[b] In parentheses, literature data (reaction time and adducts yield) for the process in organic solvents (THF,[1d,e,m,2a] benzene,[1k] CH_2Cl_2,[1f,l] 1,4-dioxane[1b,c]) are given.

Nonequivalence of signals of two phenyl or phenylethyl groups in the ^1H and ^{13}C NMR spectra of phosphine chalcogenides is caused by the presence of a chiral carbon atom in the HOCHP=X fragment.

The structures of α-hydroxyphosphine chalcogenides **12a**–**l** and **18a**–**m** have been elucidated by multinuclear ^1H, ^{13}C, ^{15}N, ^{31}P, ^{77}Se NMR spectroscopy and X-ray diffraction analysis. Three crystal structures are presented here: **12l** (Figure 1), **18d** (Figure 2), and **18m** (Figure 3).

The α-hydroxyphosphine chalcogenides **12**, **18** prepared are prospective building blocks for organic synthesis. Thus, the secondary alcohol **12d** is easily (r.t., 5 h, THF) vinylated by methyl propiolate in the presence of triethylamine to afford the highly functionalized acrylate **19** in 88% yield (Scheme 1).

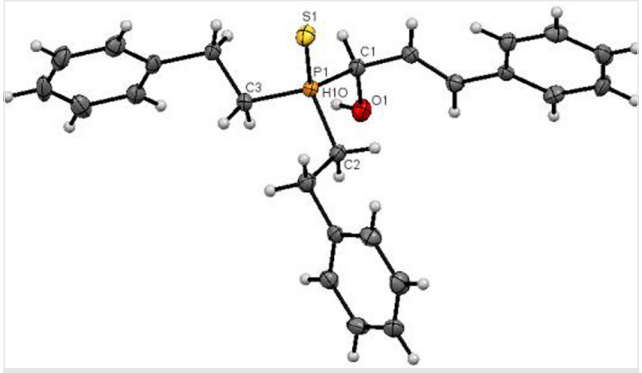
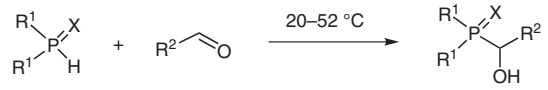


Figure 1 ORTEP diagram of the molecular structure of α-hydroxyphosphine sulfide **12l**

Table 2 Solvent-Free Synthesis of New Tertiary α-Hydroxyphosphine Chalcogenides **18a–m**[a]



1, 3, 13–16 **4–6, 10, 11, 17** **18a–m**

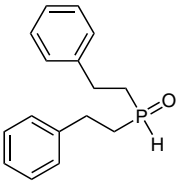
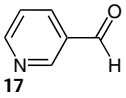
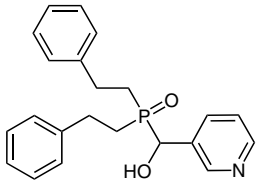
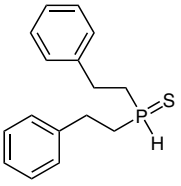
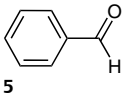
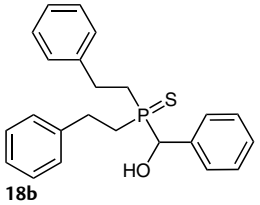
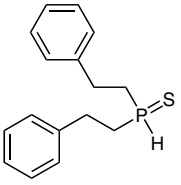
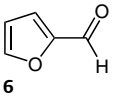
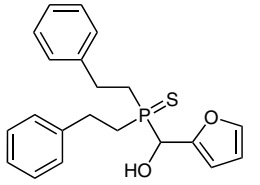
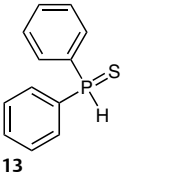
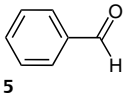
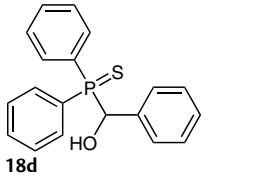
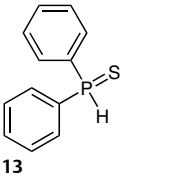
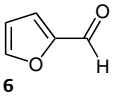
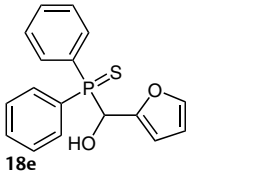
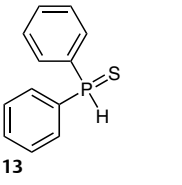
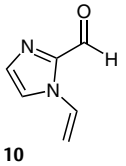
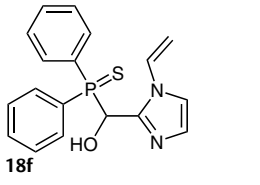
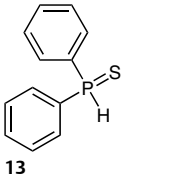
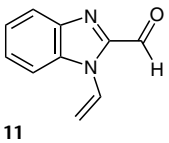
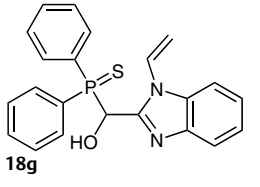
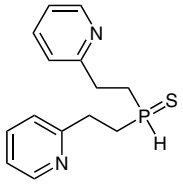
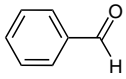
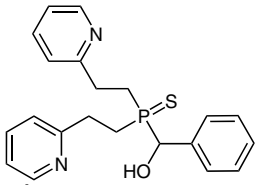
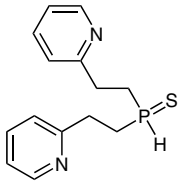
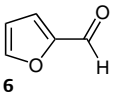
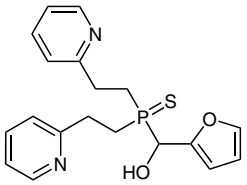
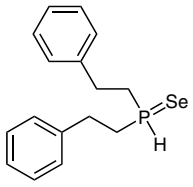
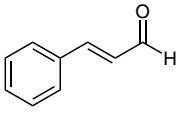
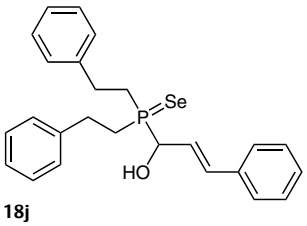
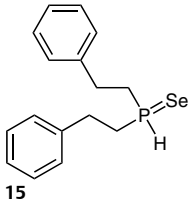
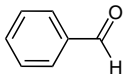
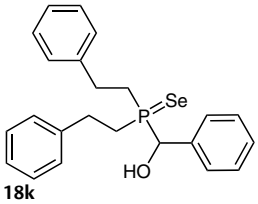
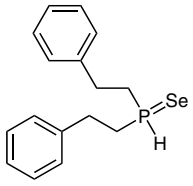
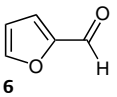
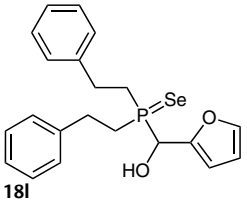
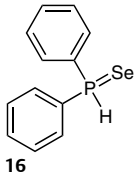
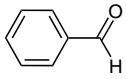
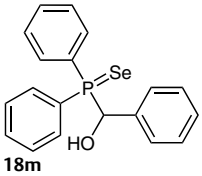
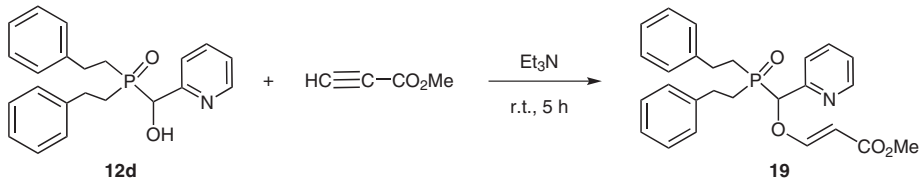
Entry	Phosphine chalcogenide	Aldehyde	Temp (°C)	Reaction time	Product **18a–m**	Isolated yield (%)
1	 **1**	 **17**	20–22	1.5 h	 **18a**	98
2	 **3**	 **5**	50–52	3 h	 **18b**	97
3	 **3**	 **6**	50–52	3 h	 **18c**	97
4	 **13**	 **5**	20–22	25 min	 **18d**	98
5	 **13**	 **6**	20–22	2 h	 **18e**	96
6	 **13**	 **10**	20–22	45 min	 **18f**	97
7	 **13**	 **11**	50–52	4 h	 **18g**	96

Table 2 (continued)

Entry	Phosphine chalcogenide	Aldehyde	Temp (°C)	Reaction time	Product **18a–m**	Isolated yield (%)
8	 **14**	 **5**	50–52	1 h	 **18h**	97
9	 **14**	 **6**	50–52	1 h	 **18i**	97
10	 **15**	 **4**	50–52	4 h	 **18j**	96
11	 **15**	 **5**	50–52	4 h	 **18k**	97
12	 **15**	 **6**	50–52	5 h	 **18l**	97
13	 **16**	 **5**	20–22	35 min	 **18m**	98

[a] Standard reaction condition: molar ratio phosphine chalcogenides **1**–**3**, **13**–**16**/aldehydes **4**–**6**, **10**, **11**, **17** = 1:1, argon.

In summary, catalyst- and solvent-free click method for the synthesis of α-hydroxyphosphine chalcogenides via the atom-economic quantitative addition of secondary phosphine chalcogenides to diverse aldehydes under room temperature or mild heating has been developed. The α-hydroxyphosphine chalcogenides prepared are reactive building blocks for organic synthesis, promising ligands in transition-metal catalysis, flame retardants for polymeric materials, and prospective precursors for design of antiviral drugs.



12d 19

Scheme 1 Reaction of α-hydroxyphosphine oxide **12d** with methyl propiolate

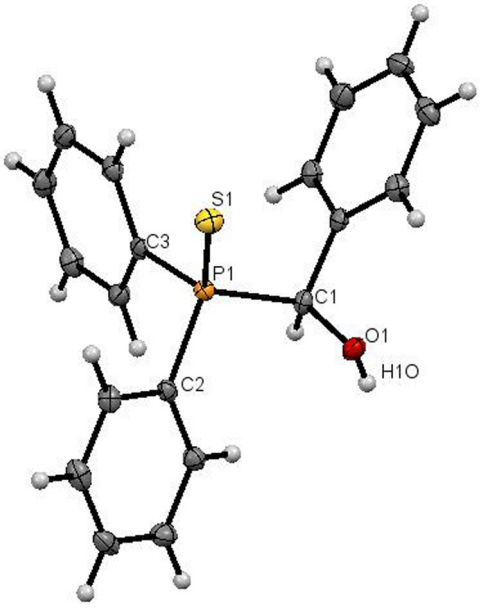


Figure 2 ORTEP diagram of the molecular structure of α-hydroxyphosphine sulfide **18d**

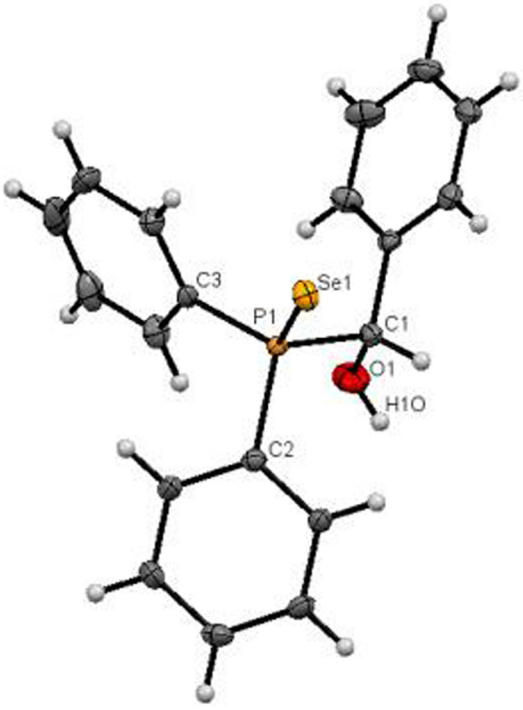


Figure 3 ORTEP diagram of the molecular structure of α-hydroxyphosphine selenide **18m**

All reactions were carried out under an argon atmosphere. Commercially available (Aldrich) diphenylphosphine oxide (**2**) and aldehydes **4**–**8** were used as received. Aldehydes **9**–**11** were prepared according to the literature protocol.[10] Diphenylphosphine sulfide (**13**) and diphenylphosphine selenide (**16**) were prepared by oxidation of commercially available diphenylphosphine (Aldrich) with elemental sulfur or selenium.[11] Secondary phosphine chalcogenides **1**, **3**, **14**, and **15** were prepared from styrene or 2-vinylpyridine and elemental phosphorus as previously reported.[8] The reaction was monitored using ^{31}P NMR spectroscopy by the disappearance of peaks of the initial secondary phosphine chalcogenides **1**–**3**, **13**–**16** (δ_P = 2.2–32.4) and appearance of new peaks corresponding to α-hydroxyphosphine chalcogenides **12a**–**l** and **18a**–**m** (δ_P = ~28–61). The ^{1}H, ^{13}C, ^{15}N, ^{31}P, and ^{77}Se NMR spectra were recorded on Bruker DPX 400 and Bruker AV-400 spectrometers (400.13, 100.61, 40.56, 161.98, and 76.31 MHz, respectively) in $CDCl_3$ and DMSO-d_6 solutions and referenced to TMS (^{1}H NMR, ^{13}C NMR), $MeNO_2$ (^{15}N NMR), H_3PO_4 (^{31}P NMR), and Me_2Se (^{77}Se NMR). The values of the δ ^{15}N were measured through the 2D ^{1}H-^{15}N HMBC experiment. Coupling constants are given in hertz. All 2D NMR spectra were recorded by using a standard gradient Bruker pulse programs. HSQC spectra via double INEPT transfer in the phase-sensitive TPPI mode with GARP decoupling during acquisition were recorded.[12] HMBC spectra were obtained with the inverse technique and processed in the magnitude mode.[13] IR spectra were recorded on a Bruker Vertex 70 instrument. Melting points were recorded on a Stuart melting point apparatus and are uncorrected. The microanalyses were performed on a Flash EA 1112 Series elemental analyzer.

X-ray Crystallographic Data[14]

Data were collected on a Bruker D8 Venture Photon 100 CMOS diffractometer with MoKα radiation (λ = 0.71073 Å) using the ϕ and ω scan techniques. The structures were solved and refined by direct methods using the SHELX.[15] Data were corrected for absorption effects using the multi-scan method (SADABS). All non-hydrogen atoms were refined anisotropically using SHELX.[15] The coordinates of the hydrogen atoms were calculated from geometrical positions (for compound **18m**); in all other cases a mixed method was used.

α-Hydroxyphosphine Chalcogenides 12a–l and 18a–m; General Procedure

A mixture of respective secondary phosphine chalcogenide **1**–**3**, **13**–**16** (1 mmol) and the appropriate aldehyde **4**–**11** (1 mmol) was stirred at 20–52 °C for 10 min to 5 h (Tables 1, 2). The residue was recrystallized from hexane and dried under vacuum to afford the proper α-hydroxyphosphine chalcogenides **12a–l** and **18a–m**.

(2*E*)-1-[Bis(2-phenylethyl)phosphoryl]-3-phenylprop-2-en-1-ol (12a)

Prepared from **1** (258 mg, 1 mmol) and **4** (132 mg, 1 mmol); yield: 374 mg (96%); white powder; mp 161–162 °C (hexane).

IR (KBr): 3106 (OH), 1143 cm^{-1} (P=O).

^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.97–2.13, 2.19–2.29 (m, 4 H, CH_2P), 2.89–2.98, 3.00–3.05 (m, 4 H, PhCH_2), 4.75 (dd, $^3J_{HH}$ = 6.4 Hz, $^2J_{HP}$ = 9.1 Hz, 1 H, PCH), 6.31, 6.36 (2 dd, $^3J_{HH}$ = 15.9 Hz, $^3J_{HH}$ = 6.4 Hz, $^3J_{HP}$ = 4.0 Hz, 1 H, =CH), 6.74, 6.78 (2 d, $^3J_{HH}$ = 15.9 Hz, $^4J_{HP}$ = 3.4 Hz, 1 H, =CHPh), 7.15 (d, $^3J_{HH}$ = 7.3 Hz, 4 H, H_o, $C_6H_5CH_2$), 7.27–7.29 (m, 9 H, H_m, H_p, $C_6H_5CH_2$, C_6H_5C=), 7.34 (d, $^3J_{HH}$ = 7.2 Hz, 2 H, H_o, C_6H_5C=).

^{13}C NMR (100.61 Hz, $CDCl_3$): δ = 26.9 (d, $^1J_{CP}$ = 38.5 Hz, CH_2P), 27.5 (d, $^1J_{CP}$ = 37.4 Hz, CH_2P), 27.55, 27.6 (2 d, $^2J_{PC}$ = 4.0 Hz, PhCH_2), 71.3 (d, $^1J_{CP}$ = 76.7 Hz, PCH), 124.0 (d, $^2J_{CP}$ = 1.5 Hz, PCC=), 126.5, 126.6 (C_m, C_6H_5C=), 126.69, 126.7 (C_o, C_6H_5C=), 128.1 (C_p, C_6H_5C=), 128.2 (C_o, $C_6H_5CH_2$), 128.7 (C_m, $C_6H_5CH_2$), 128.8 (C_p, $C_6H_5CH_2$), 132.6 (d, $^3J_{CP}$ = 10.4 Hz, PhC=), 136.2 (d, $^4J_{CP}$ = 2.7 Hz, C_{ipso}, C_6H_5C=), 141.1, 141.7 (2 d, $^3J_{PC}$ = 12.5 Hz, C_{ipso}, $C_6H_5CH_2$).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 50.4.

Anal. Calcd for $C_{25}H_{27}O_2P$: C, 76.90; H, 6.97; P, 7.93. Found: C, 76.85; H, 6.92; P, 7.89.

[Bis(2-phenylethyl)phosphoryl](phenyl)methanol (12b)

Prepared from **1** (258 mg, 1 mmol) and **5** (106 mg, 1 mmol); yield: 353 mg (97%); white powder; mp 144–145 °C (hexane).

IR (KBr): 3168 (OH), 1139 cm^{-1} (P=O).

^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.84–2.10 (m, 4 H, CH_2P), 2.82–2.84 (m, 4 H, PhCH_2), 4.14 (br s, 1 H, OH), 5.06 (d, $^2J_{HP}$ = 6.5 Hz, 1 H, PCH), 7.10 (br s, 4 H, H_o, $C_6H_5CH_2$), 7.14–7.20 (m, 2 H, H_p, $C_6H_5CH_2$), 7.23–7.32 (m, 5 H, H_p, C_6H_5CHOH, H_m, $C_6H_5CH_2$), 7.36 (dd, $^3J_{HH}$ = 7.4 Hz, 2 H, H_m, C_6H_5CHOH), 7.44 (d, $^3J_{HH}$ = 7.0 Hz, 2 H, H_o, C_6H_5CHOH).

^{13}C NMR (100.61 Hz, $CDCl_3$): δ = 26.4 (d, $^1J_{PC}$ = 59.5 Hz, CH_2P), 26.5 (d, $^1J_{CP}$ = 60.4 Hz, CH_2P), 27.0 (PhCH_2), 71.9 (d, $^1J_{CP}$ = 75.0 Hz, PCH), 125.9 (C_o, C_6H_5CHOH), 126.0, 126.1 (C_p, $C_6H_5CH_2$), 127.6, 127.7 (C_o, $C_6H_5CH_2$), 128.17–128.21 (m, C_m, C_p, C_6H_5CHOH, C_m, $C_6H_5CH_2$), 136.7 (C_{ipso}, C_6H_5CHOH), 140.7 (d, $^3J_{CP}$ = 13.8 Hz, C_{ipso}, $C_6H_5CH_2$).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 50.0.

Anal. Calcd for $C_{23}H_{25}O_2P$: C, 75.80; H, 6.91; P, 8.50. Found: C, 75.68; H, 6.89; P, 8.44.

[Bis(2-phenylethyl)phosphoryl](2-furyl)methanol (12c)

Prepared from **1** (258 mg, 1 mmol) and **6** (96 mg, 1 mmol); yield: 347 mg (98%); white powder; mp 83–84 °C (hexane).

IR (KBr): 3149 (OH), 1148 cm^{-1} (P=O).

^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.87–1.97, 2.01–2.09 (m, 4 H, CH_2P), 2.79–2.95 (m, 4 H, PhCH_2), 5.04 (br s, 1 H, OH), 5.12 (d, $^2J_{HP}$ = 6.6 Hz, 1 H, PCH), 6.40 (dd, $^3J_{HH}$ = 3.4 Hz, $^3J_{HH}$ = 1.8 Hz, 1 H, H-4, furyl), 6.48 (dd, $^3J_{HP}$ = 2.8 Hz, $^3J_{HH}$ = 3.4 Hz, 1 H, H-3, furyl), 7.10–7.30 (m, 10 H, 2 × C_6H_5), 7.42 (dd, $^3J_{HH}$ = 1.8 Hz, $^5J_{PH}$ = 3.9 Hz, 1 H, H-5, furyl).

^{13}C NMR (100.61 Hz, $CDCl_3$): δ = 27.0 (d, $^1J_{CP}$ = 59.9 Hz, CH_2P), 27.4 (2 d, $^1J_{CP}$ = 3.4 Hz, PhCH_2), 67.2 (d, $^1J_{CP}$ = 77.6 Hz, PCH), 109.7 (d, $^3J_{CP}$ = 6.0 Hz, C-3, furyl), 111.1 (C-4, furyl), 126.4, 126.5 (C_p, C_6H_5), 128.2 (C_o, C_6H_5), 128.68, 128.7 (C_m, C_6H_5), 141.0 (d, $^3J_{CP}$ = 13.4 Hz, C_{ipso}, C_6H_5), 141.3 (d, $^3J_{CP}$ = 13.4 Hz, C_{ipso}, C_6H_5), 142.8 (C-5, furyl), 150.5 (C-2, furyl).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 49.4.

Anal. Calcd for $C_{21}H_{23}O_3P$: C, 71.17; H, 6.54; P, 8.74. Found: C, 71.08; H, 6.51; P, 8.70.

[Bis(2-phenylethyl)phosphoryl](pyridin-2-yl)methanol (12d)

Prepared from **1** (258 mg, 1 mmol) and **7** (107 mg, 1 mmol); yield: 358 mg (98%); white powder; mp 106–107 °C (hexane).

IR (KBr): 3140 (OH), 1146 cm^{-1} (P=O).

^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.71–1.88 (m, 2 H, CH_2P), 2.13–2.31 (m, 1 H, PhCH_2), 2.35–2.42 (m, 1 H, CH_2P, 1 H, PhCH_2), 2.59–2.69 (m, 1 H, CH_2P), 3.05–3.12 (m, 2 H, PhCH_2), 5.19 (d, $^2J_{HP}$ = 7.7 Hz, 1 H, PCH), 5.31 (br s, 1 H, OH), 6.99 (d, $^3J_{HH}$ = 7.7 Hz, 2 H_o, C_6H_5), 7.13–7.30 (m, 9 H, 2 H_o, 4 H_m, 2 H_p, C_6H_5 + 1 H, H-5, Py), 7.18–7.79 (m, 2 H, H-3,4, Py), 8.57 (d, $^3J_{HH}$ = 4.9 Hz, H-4, Py).

^{13}C NMR (100.61 Hz, $CDCl_3$): δ = 26.4 (d, $^1J_{PC}$ = 60.0 Hz, CH_2P), 27.2, 27.4 (2 d, $^2J_{PC}$ = 3.5 Hz, PhCH_2), 28.4 (d, $^1J_{PC}$ = 61.2 Hz, CH_2P), 70.4 (d, $^1J_{PC}$ = 74.7 Hz, PCH), 122.6 (d, $^1J_{PC}$ = 2.6 Hz, C-3, Py), 123.3 (d, $^5J_{CP}$ = 1.9 Hz, C-5, Py), 126.3, 126.4 (C_p, C_6H_5), 128.0, 128.1 (C_o, C_6H_5), 128.6, 128.7 (C_m, C_6H_5), 137.2 (d, $^4J_{PC}$ = 1.9 Hz, C-4, Py), 141.2 (d, $^3J_{CP}$ = 13.6 Hz, C_{ipso}, C_6H_5), 147.9 (d, $^4J_{CP}$ = 1.8 Hz, C-6, Py), 154.2 (C-2, Py).

^{15}N NMR (40.56 MHz, $CDCl_3$): δ = –86.9.

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 50.9.

Anal. Calcd for $C_{22}H_{24}NO_2P$: C, 72.31; H, 6.62; N, 3.83; P, 8.48. Found: C, 72.27; H, 6.59; N, 3.79; P, 8.44.

[Bis(2-phenylethyl)phosphoryl](pyridin-4-yl)methanol (12e)

Prepared from **1** (258 mg, 1 mmol) and **8** (107 mg, 1 mmol); yield: 354 mg (97%); white powder; mp 153–154 °C (hexane).

IR (KBr): 3139 (OH), 1141 cm^{-1} (P=O).

^1H HMR ($CDCl_3$): δ = 1.80–1.91, 1.90–2.10, 2.20–2.30 (m, 4 H, CH_2P), 2.45–2.56 (m, 4 H, PhCH_2), 5.05 (d, $^2J_{HP}$ = 11.9 Hz, 1 H, PCH), 6.00 (br s, 1 H, OH), 7.00 (d, $^3J_{HH}$ = 7.0 Hz, 2 H_o, C_6H_5), 7.12 (d, $^3J_{HH}$ = 7.1 Hz, 2 H_o, C_6H_5), 7.13–7.39 (m, 6 H, 4 H_m, 2 H_p, C_6H_5), 7.40 (d, $^3J_{HH}$ = 3.4 Hz, 2 H, H-3,5, Py), 8.40 (d, $^3J_{HH}$ = 3.4 Hz, 2 H, H-2,6 Py).

^{13}C NMR (100.61 Hz, $CDCl_3$): δ = 25.9 (d, $^1J_{CP}$ = 59.0 Hz, CH_2P), 27.2, 27.3 (2 d, $^2J_{CP}$ = 3.0 Hz, PhCH_2), 27.4 (d, $^1J_{PC}$ = 61.2 Hz, CH_2P), 70.0 (d, $^1J_{CP}$ = 76.2 Hz, PCH), 121.6 (C-3,5, Py), 126.57, 126.6 (C_p, C_6H_5), 128.0, 128.1 (C_o, C_6H_5), 128.7, 128.8 (C_m, C_6H_5), 140.7 (2 d, $^3J_{PC}$ = 12.2 Hz, C_{ipso}, C_6H_5), 148.1 (C-4, Py), 149.0 (C-2,6, Py).

^{15}N NMR (40.56 MHz, $CDCl_3$): δ = –77.4.

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 51.2.

Anal. Calcd for $C_{22}H_{24}NO_2P$: C, 72.31; H, 6.62; N, 3.83; P, 8.48. Found: C, 72.29; H, 6.59; N, 3.81; P, 8.43.

(2*E*)-1-(Diphenylphosphoryl)-3-phenylprop-2-en-1-ol (12f)

Prepared from **2** (202 mg, 1 mmol) and **4** (132 mg, 1 mmol); yield: 324 mg (97%); white powder; mp 147–148 °C (hexane).

IR (KBr): 3147 (OH), 1151 cm^{-1} (P=O).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 5.22 (dd, $^3J_{HH}$ = 6.2 Hz, $^2J_{HP}$ = 9.0 Hz, 1 H, PCH), 6.29, 6.33 (2 dd, $^3J_{HH}$ = 15.8 Hz, $^3J_{HH}$ = 6.2 Hz, $^3J_{HP}$ = 5.1 Hz, 1 H, =CH), 6.39 (br s, 1 H, OH), 6.52, 6.57 (2 d, $^3J_{HH}$ = 15.8 Hz, $^4J_{HP}$ = 4.2 Hz, 1 H, =C*H*Ph), 7.18–7.19 (m, 15 H, 3 × C_6H_5).

^{13}C NMR (100.61 Hz, $CDCl_3$): δ = 71.4 (d, $^1J_{PC}$ = 87.5 Hz, PCH), 125.9 (PCHC=), 126.2 (C_m, C_6H_5C=), 127.7 (C_p, C_6H_5C=), 128.3 (d, $^3J_{CP}$ = 11.2 Hz, C_m, C_6H_5P), 128.5 (d, $^3J_{PC}$ = 10.8 Hz, C_m, C_6H_5P), 131.3 (C_o, C_6H_5C=), 131.7 (d, $^2J_{CP}$ = 8.2 Hz, C_o, C_6H_5P), 132.0 (d, $^3J_{CP}$ = 10.3 Hz, PhC=), 132.1 (m, C_o, C_p, C_6H_5P), 132.7 (d, $^1J_{CP}$ = 92.7 Hz, C_{ipso}, C_6H_5P), 136.3 (C_{ipso}, C_6H_5C=).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 29.1.

Anal. Calcd for $C_{21}H_{19}O_2P$: C, 75.44; H, 5.73; P, 9.26. Found: C, 75.29; H, 5.69; P, 9.19.

(Diphenylphosphoryl)(phenyl)methanol (12g)

Prepared from **2** (202 mg, 1 mmol) and **5** (106 mg, 1 mmol); yield: 302 mg (98%); white powder; mp 152–153 °C (hexane).

IR (KBr): 3182 (OH), 1163 cm^{-1} (P=O).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 5.42 (d, $^2J_{PH}$ = 8.9 Hz, 1 H, PCH), 6.24 (br s, 1 H, OH), 7.12–7.17 (m, 5 H, C_6H_5CHOH), 7.32–7.38, 7.43–7.45 (m, 6 H, 4 H_m, 2 H_p, C_6H_5P), 7.73, 7.80 (2 dd, $^3J_{HH}$ = 7.9 Hz, $^3J_{PH}$ = 11.0 Hz, 4 H, H_o, C_6H_5P).

^{13}C NMR (100.61 Hz, $CDCl_3$): δ = 72.5 (d, $^1J_{CP}$ = 86.2 Hz, PCH), 127.1 (C_m, C_6H_5CHOH), 127.1 (C_p, C_6H_5CHOH), 127.2 (C_o, C_6H_5CHOH), 127.5 (d, $^3J_{CP}$ = 11.6 Hz, C_m, C_6H_5P), 127.8 (d, $^3J_{PC}$ = 11.2 Hz, C_m, C_6H_5P), 129.4 (d, $^1J_{CP}$ = 95.7 Hz, C_{ipso}, C_6H_5P), 131.2 (C_p, C_6H_5P), 131.3 (C_p, C_6H_5P), 131.3 (d, $^2J_{CP}$ = 8.6 Hz, C_o, C_6H_5P), 131.9 (d, $^2J_{CP}$ = 8.6 Hz, C_o, C_6H_5P), 132.0 (d, $^1J_{CP}$ = 95.7 Hz, C_{ipso}, C_6H_5P), 137.2 (C_{ipso}, C_6H_5CHOH).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 28.6.

Anal. Calcd for $C_{19}H_{17}O_2P$: C, 74.02; H, 5.56; P, 10.05. Found: C, 73.97; H, 5.53; P, 9.98.

(Diphenylphosphoryl)(2-furyl)methanol (12h)

Prepared from **2** (202 mg, 1 mmol) and **6** (96 mg, 1 mmol); yield: 292 mg (98%); yellow powder; mp 156–157 °C (hexane).

IR (KBr): 3149 (OH), 1150 cm^{-1} (P=O).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 4.98 (br s, 1 H, OH), 5.50 (d, $^2J_{HP}$ = 5.6 Hz, 1 H, PCH), 6.21 (dd, $^3J_{HH}$ = 3.6 Hz, $^3J_{HH}$ = 1.7 Hz, 1 H, H-4, furyl), 6.28 (dd, $^3J_{HH}$ = 3.6 Hz, $^4J_{HP}$ = 2.7 Hz, 1 H, H-3, furyl), 7.23 (dd, $^5J_{HP}$ = 3.2 Hz, $^3J_{HH}$ = 1.7 Hz, 1 H, H-5, furyl), 7.38, 7.45 (2 ddd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 2.8 Hz, 4 H, H_m, C_6H_5), 7.48, 7.55 (2 t, $^3J_{HH}$ = 7.6 Hz, 2 H, H_p, C_6H_5), 7.66, 7.80 (2 dd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HP}$ = 10.4 Hz, 4 H, H_o, C_6H_5).

^{13}C NMR (100.61 Hz, DMSO-d_6): δ = 67.5 (d, $^1J_{CP}$ = 83.6 Hz, PCH), 109.0 (d, $^3J_{CP}$ = 4.7 Hz, C-3, furyl), 110.2 (C-4, furyl), 127.6, 127.8 (2 d, $^1J_{PC}$ = 11.0 Hz, C_m, C_6H_5), 129.9 (d, $^1J_{CP}$ = 96.1 Hz, C_{ipso}, C_6H_5), 131.2 (d, $^2J_{CP}$ = 8.6 Hz, C_o, C_6H_5), 131.3, 131.4 (2 d, $^4J_{PC}$ = 2.6 Hz, C_p, C_6H_5), 131.6 (d, $^1J_{CP}$ = 96.1 Hz, C_{ipso}, C_6H_5), 131.8 (d, $^2J_{CP}$ = 8.6 Hz, C_o, C_6H_5).

^{31}P NMR (161.98 MHz, DMSO-d_6 + $CDCl_3$): δ = 31.1.

Anal. Calcd for $C_{17}H_{15}O_3P$: C, 68.45; H, 5.07; P, 10.38. Found: C, 68.41; H, 5.05; P, 10.34.

(Diphenylphosphoryl)(1-ethyl-1*H*-imidazol-2-yl)methanol (12i)

Prepared from **2** (202 mg, 1 mmol) and **9** (124 mg, 1 mmol); yield: 316 mg (97%); white powder; mp 138–139 °C (hexane).

IR (KBr): 2634 (OH), 1194 cm^{-1} (P=O).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.34 (t, $^3J_{HH}$ = 7.3 Hz, 3 H, CH_3), 4.08–4.20 (m, 2 H, NCH_2), 5.67 (d, $^2J_{HP}$ = 5.4 Hz, 1 H, PCH), 6.82 (d, $^3J_{HH}$ = 1.1 Hz, 1 H, H-4, imidazolyl), 6.86 (d, $^3J_{HH}$ = 1.1 Hz, $^5J_{HP}$ = 1.5 Hz, 1 H, H-5, imidazolyl), 7.35 (dt, $^3J_{HH}$ = 7.6 Hz, $^5J_{HP}$ = 2.6 Hz, 2 H, H_p, C_6H_5), 7.42–7.55 (m, 4 H, H_m, C_6H_5), 7.62 (dd, $^3J_{HH}$ = 7.7 Hz, $^3J_{HP}$ = 11.1 Hz, 2 H, H_o, C_6H_5), 7.93 (dd, $^3J_{HH}$ = 7.7 Hz, $^3J_{HP}$ = 11.1 Hz, 2 H, H_o, C_6H_5).

^{13}C NMR (100.61 Hz, $CDCl_3$): δ = 15.8 (CH_3), 41.5 (NCH_2), 67.7 (d, $^1J_{CP}$ = 84.5 Hz, PCH), 120.3 (C-5, imidazolyl), 127.2 (C-4, imidazolyl), 128.0, 128.4 (2 d, $^3J_{CP}$ = 11.6 Hz, C_m, C_6H_5), 129.5, 131.0 (2 d, $^1J_{CP}$ = 96.1 Hz, C_{ipso}, C_6H_5), 131.7, 132.2 (2 d, $^2J_{CP}$ = 9.1 Hz, C_o, C_6H_5), 132.0 (d, $^1J_{CP}$ = 1.7 Hz, C_p, C_6H_5), 142.8 (C-2, imidazolyl).

^{15}N NMR (40.56 MHz, $CDCl_3$): δ = –204.1 (N-1), –128.8 (N-3).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 31.6.

Anal. Calcd for $C_{18}H_{19}N_2O_2P$: C, 66.25; H, 5.87; N, 8.58; P, 9.49. Found: C, 66.21; H, 5.86; N, 8.57; P, 9.45.

(Diphenylphosphoryl)(1-vinyl-1*H*-imidazol-2-yl)methanol (12j)

Prepared from **2** (202 mg, 1 mmol) and **10** (122 mg, 1 mmol); yield: 311 mg (96%); yellow powder; mp 145–146 °C (hexane).

IR (KBr): 2690 (OH), 1204 cm^{-1} (P=O).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 4.86 (d, $^3J_{HH}$ = 8.4 Hz, 1 H, =CH_2), 5.16 (d, $^3J_{HH}$ = 15.4 Hz, 1 H, =CH_2), 5.69 (d, $^2J_{HP}$ = 5.3 Hz, 1 H, PCH), 6.83 (s, 1 H, H-4, imidazolyl), 7.18 (s, 1 H, H-5, imidazolyl), 7.37–7.54 (m, 7 H, 4 H_m, 2 H_p, C_6H_5 + 1 H, =CH), 7.65 (dd, $^3J_{HH}$ = 8.6 Hz, $^3J_{HP}$ = 11.9 Hz, 2 H, H_o, C_6H_5), 7.91 (dd, $^3J_{HH}$ = 8.6 Hz, $^3J_{HP}$ = 12.0 Hz, 2 H, H_o, C_6H_5).

^{13}C NMR (100.61 Hz, $CDCl_3$): δ = 63.2 (d, $^1J_{CP}$ = 83.6 Hz, PCH), 98.2 (=CH_2), 112.64 (C-5, imidazolyl), 123.3 (C-4, imidazolyl), 123.4 (d, $^1J_{CP}$= 12.1 Hz, C_m, C_6H_5), 123.7 (d, $^1J_{CP}$ = 11.6 Hz, C_m, C_6H_5), 124.0 (d, $^1J_{CP}$ = 97.8 Hz, C_{ipso}, C_6H_5), 125.1 (CH=), 125.7 (d, $^1J_{CP}$ = 97.0 Hz, C_{ipso}, C_6H_5), 126.9 (d, $^1J_{CP}$ = 9.0 Hz, C_o, C_6H_5), 127.4–127.5 (m, C_o, C_p, C_6H_5), 138.3 (C-2, imidazolyl).

^{15}N NMR (40.56 MHz, $CDCl_3$): δ = –197.1 (N-1), –124.1 (N-3).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 31.6.

Anal. Calcd for $C_{18}H_{17}N_2O_2P$: C, 66.66; H, 5.28; N, 8.64; P, 9.55. Found: C, 66.62; H, 5.27; N, 8.64; P, 9.52.

(Diphenylphosphoryl)(1-vinyl-1*H*-benzimidazol-2-yl)methanol (12k)

Prepared from **2** (202 mg, 1 mmol) and **11** (172 mg, 1 mmol); yield: 363 mg (97%); yellow powder; mp 184–185 °C (hexane).

IR (KBr): 3130 (OH), 1190 cm^{-1} (P=O).

^{1}H NMR (400.13 MHz, DMSO-d_6): δ = 5.14 (d, $^3J_{HH}$ = 9.1 Hz, 1 H, =CH_2), 5.57 (d, $^3J_{HH}$ = 16.1 Hz, 1 H, =CH_2), 6.12 (dd, $^3J_{HH}$ = 5.3 Hz, $^2J_{HP}$ = 8.2 Hz, 1 H, PCH), 6.98 (dd, $^3J_{HH}$ = 5.3 Hz, $^3J_{HP}$ = 15.8 Hz, 1 H, OH), 7.22 (dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 8.8 Hz, 1 H_{arom}, H-5), 7.29 (dd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 8.8 Hz, 1 H_{arom}, H-6), 7.47–7.60 (m, 8 H, 4 H_m, 2 H_p, C_6H_5, + 1 H_{arom}, H-4, + 1 H, =CH), 7.71 (d, $^3J_{HH}$ = 7.8 Hz, 1 H_{arom}, H-7), 7.82, 7.90 (2 ddd, $^3J_{HH}$ = 8.6 Hz, $^3J_{HP}$ = 11.6 Hz, 4 H, H_o, C_6H_5).

^{13}C NMR (100.61 Hz, $CDCl_3$): δ = 68.0 (d, $^1J_{PC}$ = 81.0 Hz, PCH), 109.9 (=CH_2), 111.8 (C-7, Ar), 119.6 (C-4, Ar), 123.2 (C-5, Ar), 123.9 (C-6, Ar), 128.3, 128.8 (2 d, $^3J_{CP}$ = 12.1 Hz, C_m, C_6H_5), 128.6 (d, $^1J_{CP}$ = 91.4 Hz, C_{ipso}, C_6H_5), 129.7 (CH=), 130.8 (d, $^1J_{CP}$ = 96.9 Hz, C_{ipso}, C_6H_5), 131.9 (d, $^2J_{CP}$ = 9.1 Hz, C_o, C_6H_5), 132.3 (d, $^4J_{CP}$ = 2.6 Hz, C_o, C_6H_5), 132.6 (C_p, C_6H_5), 132.7 (d, $^2J_{CP}$ = 9.1 Hz, C_o, C_6H_5), 134.8 (C-9, Ar), 141.9 (C-8, Ar), 150.0 (C=N).

^{15}N NMR (40.56 MHz, $CDCl_3$): δ = –216.8 (N-1), –138.4 (N-3).

^{31}P NMR (161.98 MHz, DMSO-d_6): δ = 32.4.

Anal. Calcd for $C_{22}H_{19}N_2O_2P$: C, 70.58; H, 5.12; N, 7.48; P, 8.27. Found: C, 70.55; H, 5.10; N, 7.49; P, 8.24.

(2*E*)-1-[Bis(2-phenylethyl)phosphorothioyl]-3-phenylprop-2-en-1-ol (12l)

Prepared from **3** (274 mg, 1 mmol) and **4** (132 mg, 1 mmol); yield: 390 mg (96%); yellow powder; mp 126–127 °C (hexane).

IR (KBr): 3271 (OH), 599 cm^{-1} (P=S).

^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.97–2.07, 2.09–2.27 (m, 4 H, CH_2P), 2.91–3.02 (m, 4 H, PhCH_2), 4.46 (ddd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HH}$ = 1.3 Hz, $^2J_{HP}$ = 3.1 Hz, 1 H, PCH), 6.24 (ddd, $^3J_{HH}$ = 15.8 Hz, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 4.2 Hz, 1 H, =CH), 6.69 (dd, $^3J_{HH}$ = 15.8 Hz, $^4J_{HP}$ = 4.2 Hz, 1 H, =C*H*Ph), 7.13 (d, $^3J_{HH}$ = 7.1 Hz, 2 H, H_o, $C_6H_5CH_2$), 7.27–7.29 (m, 13 H, 4 H, H_o, 6 H, H_m, 3 H, H_p, $C_6H_5CH_2$, C_6H_5C=).

^{13}C NMR (100.61 Hz, $CDCl_3$): δ = 28.5, 28.6 (2 d, $^2J_{CP}$ = 3.0 Hz, PhCH_2), 29.6, 30.0 (2 d, $^1J_{CP}$ = 44.8 Hz, CH_2P), 72.3 (d, $^1J_{CP}$ = 54.3 Hz, PCH), 123.1 (d, $^2J_{CP}$ = 3.5 Hz, PCHC=), 126.6 (C_p, PhC=), 126.81–126.83 (m, C_o, C_m, C_6H_5C=), 128.35, 128.4 (C_m, $C_6H_5CH_2$), 128.5 (C_p, $C_6H_5CH_2$), 128.78, 128.8 (C_o, $C_6H_5CH_2$), 133.7 (d, $^3J_{CP}$ = 11.2 Hz, C_6H_5C=), 135.8 (d, $^4J_{CP}$ = 2.6 Hz, C_{ipso}, C_6H_5C=), 140.7 (dd, $^3J_{CP}$ = 13.4 Hz, C_{ipso}, $C_6H_5CH_2$).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 57.9.

Anal. Calcd for $C_{25}H_{27}OPS$: C, 73.86; H, 6.69; P, 7.62; S, 7.89. Found: C, 73.42; H, 6.61; P, 6.99; S, 7.79.

[Bis(2-phenylethyl)phosphoryl](pyridin-3-yl)methanol (18a)

Prepared from **1** (258 mg, 1 mmol) and **17** (107 mg, 1 mmol); yield: 358 mg (98%); white powder; mp 101–102 °C (hexane).

IR (KBr): 3139 (OH), 1140 cm^{-1} (P=O).

^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.89–1.99 (m, 4 H, CH_2P), 2.09–2.19 (m, 4 H, PhCH_2), 5.06 (d, $^2J_{HP}$ = 8.2 Hz, 1 H, PCH), 7.05, 7.10 (2 d, $^3J_{HH}$ =7.8 Hz, 4 H, H_o, C_6H_5), 7.17–7.26 (m, 6 H, H_m, H_p, C_6H_5), 7.84 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, H-4, Py), 8.48 (d, $^3J_{HH}$ = 3.4 Hz, 1 H, H-6, Py), 8.63 (H-2, Py).

^{13}C NMR (100.61 Hz, $CDCl_3$): δ = 25.8 (d, $^1J_{CP}$ = 59.6 Hz, CH_2P), 27.4 (d, $^1J_{CP}$ = 60.9 Hz, CH_2P), 27.5 (PhCH_2), 69.1 (d, $^1J_{CP}$ = 78.1 Hz, PCH), 123.4 (C-5, Py), 126.5, 126.6 (C_p, C_6H_5), 128.0, 128.1 (C_o, C_6H_5), 128.7 (C_m, C_6H_5), 133.9 (C-6, Py), 134.8 (C-1, Py), 140.7, 140.8 (2 d, $^3J_{CP}$ = 9.4 Hz, C_{ipso}, C_6H_5), 147.4 (C-2, Py), 148.7 (C-4, Py).

^{15}N NMR (40.56 MHz, $CDCl_3$): δ = –73.4.

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 51.4.

Anal. Calcd for $C_{22}H_{24}NO_2P$: C, 72.31; H, 6.62; N, 3.83; P, 8.48. Found: C, 72.27; H, 6.60; N, 3.82; P, 8.45.

[Bis(2-phenylethyl)phosphorothioyl](phenyl)methanol (18b)

Prepared from **3** (274 mg, 1 mmol) and **5** (106 mg, 1 mmol); yield: 369 mg (97%); white powder; mp 111–112 °C (hexane).

IR (KBr): 3305 (OH), 592 cm^{-1} (P=S).

^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.69–1.79, 1.88–1.96, 2.04–2.23 (m, 4 H, CH_2P), 2.59–2.62, 2.71–2.73, 2.91–2.98 (m, 4 H, PhCH_2), 3.76 (br s, 1 H, OH), 4.87 (s, 1 H, PCH), 7.00 (d, $^3J_{HH}$ = 7.5 Hz, 2 H, H_o, C_6H_5CHOH), 7.15–7.22 (m, 4 H, H_m, 2 H, H_p, $C_6H_5CH_2$), 7.28 (dd, $^3J_{HH}$ = 8.9 Hz, $^3J_{HH}$ = 7.5 Hz, 2 H, H_m, C_6H_5CHOH), 7.33–7.39 (m, 4 H, H_o, $C_6H_5CH_2$, 1 H, H_p, C_6H_5CHOH).

^{13}C NMR (100.61 Hz, $CDCl_3$): δ = 28.4, 28.6 (2 d, $^2J_{PC}$ = 3.0 Hz, PhCH_2), 29.2, 30.4 (d, $^1J_{CP}$ = 44.4 Hz, CH_2P), 72.7 (d, $^1J_{CP}$ = 49.6 Hz, PCH), 126.5 (C_p, $C_6H_5CH_2$), 126.69 (d, $^3J_{CP}$ = 4.7 Hz, C_o, C_6H_5CHOH), 126.7 (C_p, $C_6H_5CH_2$), 128.2 (C_m, $C_6H_5CH_2$), 128.4 (C_m, $C_6H_5CH_2$), 128.7 (C_o, $C_6H_5CH_2$), 128.81 (d, $^4J_{CP}$ = 2.6 Hz, C_m, C_6H_5CHOH), 128.82 (C_o, $C_6H_5CH_2$), 128.9 (d, $^5J_{CP}$ = 3.0 Hz, C_p, C_6H_5CHOH), 136.2 (d, $^2J_{CP}$ = 2.2 Hz, C_{ipso}, C_6H_5CHOH), 140.6, 140.7 (2 d, $^3J_{CP}$ = 13.8 Hz, $^3J_{PC}$ = 14.7 Hz, C_{ipso}, $C_6H_5CH_2$).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 59.3.

Anal. Calcd for $C_{23}H_{25}OPS$: C, 72.60; H, 6.62; P, 8.14; S, 8.43. Found: C, 72.57; H, 6.61; P, 8.09; S, 8.42.

[Bis(2-phenylethyl)phosphorothioyl](2-furyl)methanol (18c)

Prepared from **3** (274 mg, 1 mmol) and **6** (96 mg, 1 mmol); yield: 359 mg (97%); white powder; mp 87–88 °C (hexane).

IR (KBr): 3213 (OH), 604 cm^{-1} (P=S).

^1H NMR (400.13 MHz, $CDCl_3$): δ = 1.82–1.92, 1.96–2.07, 2.11–2.28 (m, 4 H, CH_2P), 2.68–2.81, 2.91–2.91 (m, 4 H, PhCH_2), 3.66 (br s, 1 H, OH), 4.89 (s, 1 H, PCH), 6.41 (dd, $^3J_{HH}$ = 3.4 Hz, $^3J_{HH}$ = 1.8 Hz, 1 H, H-4, furyl), 6.46 (dd, $^3J_{HP}$ = 4.2 Hz, $^3J_{HH}$ = 3.4 Hz, 1 H, H-3, furyl), 7.07 (d, $^3J_{HH}$ = 7.5 Hz, 2 H, H_o, C_6H_5), 7.12–7.30 (m, 8 H, 2 H, H_o, 4 H, H_m, 2 H, H_p, C_6H_5), 7.42 (dd, $^3J_{HH}$ = 1.8 Hz, $^5J_{PH}$ = 2.9 Hz, 1 H, H-5, furyl).

^{13}C NMR (100.61 Hz, $CDCl_3$): δ = 28.3, 28.4 (2 d, $^2J_{CP}$ = 3.0 Hz, PhCH_2), 29.8, 30.8 (2 d, $^2J_{CP}$ = 44.4 Hz, CH_2P), 67.3 (d, $^1J_{CP}$ = 53.5 Hz, PCH), 109.2 (d, $^3J_{CP}$ = 6.0 Hz, C-3, furyl), 111.2 (d, $^4J_{CP}$ = 2.2 Hz, C-4, furyl), 126.3, 126.5 (C_p, C_6H_5), 128.2, 128.4 (C_o, C_6H_5), 128.6, 128.8 (C_m, C_6H_5), 140.5 (d, $^3J_{CP}$ = 13.8 Hz, C_{ipso}, C_6H_5), 140.7 (d, $^3J_{CP}$ = 14.7 Hz, C_{ipso}, C_6H_5), 143.0 (d, $^1J_{CP}$ = 2.6 Hz, C-5, furyl), 149.5 (d, $^1J_{CP}$ = 3.0 Hz, C-2, furyl).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 59.6.

Anal. Calcd for $C_{21}H_{23}O_2PS$: C, 68.09; H, 6.26; P, 8.36; S, 8.66. Found: C, 68.08; H, 6.25; P, 8.33; S, 8.65.

(Diphenylphosphorothioyl)(phenyl)methanol (18d)[16]

Prepared from **13** (218 mg, 1 mmol) and **5** (106 mg, 1 mmol); yield: 318 mg (98%); white powder; mp 120–121 °C (hexane).

IR (KBr): 3289 (OH), 596 cm^{-1} (P=S).

^1H NMR (400.13 MHz, $CDCl_3$): δ = 3.67 (br s, 1 H, OH), 5.53 (s, 1 H, PCH), 7.04 (d, $^3J_{HH}$ = 7.6 Hz, 2 H, H_o, C_6H_5CHOH), 7.08 (dd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.6 Hz, 2 H, H_m, C_6H_5CHOH), 7.16 (t, $^3J_{HH}$ = 7.6 Hz, 1 H, H_p, C_6H_5CHOH), 7.23–7.27 (m, 2 H, H_m, C_6H_5P), 7.39 (t, $^3J_{HH}$ = 7.7 Hz, 1 H, H_p, C_6H_5P), 7.43–7.50 (m, 4H, 2 H, H_o, 2 H, H_m, C_6H_5P), 7.54 (t, $^3J_{HH}$ = 7.7 Hz, 1 H, H_p, C_6H_5P), 7.90 (dd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HP}$ = 12.3 Hz, 2 H, H_o, C_6H_5P).

^{13}C NMR (100.61 Hz, $CDCl_3$): δ = 73.5 (d, $^1J_{CP}$ = 54.3 Hz, PCH), 127.5 (d, $^3J_{CP}$ = 4.7 Hz, C_o, C_6H_5CHOH), 127.7 (d, $^4J_{CP}$ = 2.6 Hz, C_m, C_6H_5CHOH), 128.2 (d, $^3J_{CP}$ = 12.1 Hz, C_m, C_6H_5P), 128.3 (d, $^5J_{CP}$ = 3.4 Hz, C_p, C_6H_5CHOH), 128.8 (d, $^3J_{CP}$ = 12.1 Hz, C_m, C_6H_5P), 129.4 (d, $^1J_{CP}$ = 76.3 Hz, C_{ipso}, C_6H_5P), 130.6 (d, $^1J_{CP}$ = 76.7 Hz, C_{ipso}, C_6H_5P), 131.2, 132.3 (d, $^2J_{CP}$ = 9.5 Hz, C_o, C_6H_5P), 132.7 (d, $^2J_{CP}$ = 9.9 Hz, C_o, C_6H_5P), 135.8 (C_{ipso}, C_6H_5CHOH).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 53.0.

Anal. Calcd for $C_{19}H_{17}OPS$: C, 70.35; H, 5.28; P, 9.55; S, 9.89. Found: C, 70.31; H, 5.27; P, 9.52; S, 9.87.

(Diphenylphosphorothioyl)(2-furyl)methanol (18e)

Prepared from **13** (218 mg, 1 mmol) and **6** (96 mg, 1 mmol); yield: 301 mg (96%); yellow powder; mp 100–101 °C (hexane).

IR (KBr): 3272 (OH), 595 cm^{-1} (P=S).

^1H NMR (400.13 MHz, $CDCl_3$): δ = 4.01 (br s, 1 H, OH), 5.56 (s, 1 H, PCH), 6.19 (dd, $^3J_{HH}$ = 3.4 Hz, $^3J_{HH}$ = 1.8 Hz, 1 H, H-4, furyl), 6.24 (dd, $^3J_{HH}$ = 3.4 Hz, $^3J_{HH}$ = 2.7 Hz, 1 H, H-3, furyl), 7.14 (d, $^3J_{HH}$ = 1.8 Hz, 1 H,

H-5, furyl), 7.34 (ddd, $^3J_{HH}$ = 7.6 Hz, $^5J_{HP}$ = 3.9 Hz, 2 H, H_p, C_6H_5), 7.42–7.55 (m, 4 H, H_m, C_6H_5), 7.61 (dt, $^3J_{HH}$ = 7.2 Hz, $^2J_{HP}$ = 11.9 Hz, 2 H, H_o, C_6H_5), 7.90 (dt, $^3J_{HH}$ = 7.2 Hz, $^2J_{HP}$ = 11.9 Hz, 2 H, H_o, C_6H_5).

^{13}C NMR (100.61 Hz, $CDCl_3$): δ = 68.1 (d, $^1J_{CP}$ = 59.9 Hz, PCH), 109.8 (d, $^3J_{CP}$ = 5.2 Hz, C-3, furyl), 110.8 (d, $^4J_{CP}$ = 1.7 Hz, C-4, furyl), 126.9, 128.4 (2 d, $^1J_{CP}$ = 12.1 Hz, C_o, C_6H_5), 129.4 (d, $^1J_{CP}$ = 79.7 Hz, C_{ipso}, C_6H_5), 130.6 (d, $^1J_{CP}$ = 78.4 Hz, C_{ipso}, C_6H_5), 132.0–132.4 (C_m, C_p, C_6H_5), 142.5 (d, $^4J_{CP}$ = 2.6 Hz, C-5, furyl), 149.6 (C-2, furyl).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 51.2.

Anal. Calcd for $C_{17}H_{15}O_2PS$: C, 64.96; H, 4.81; P, 9.85; S, 10.20. Found: C, 64.93; H, 4.79; P, 9.81; S, 10.18.

(Diphenylphosphorothioyl)(1-vinyl-1*H*-imidazol-2-yl)methanol (18f)

Prepared from **13** (218 mg, 1 mmol) and **10** (122 mg, 1 mmol); yield: 330 mg (97%); yellow powder; mp 128–129 °C (hexane).

IR (KBr): 2685 (OH), 613 cm^{-1} (P=S).

^{1}H NMR (400.13 MHz, DMSO-d_6): δ = 4.71 (d, $^3J_{HH}$ = 8.8 Hz, 1 H, =CH_2), 5.30 (d, $^3J_{HH}$ = 15.7 Hz, 1 H, =CH_2), 6.16 (dd, $^3J_{HH}$ = 5.3 Hz, $^2J_{HP}$ = 6.7 Hz, 1 H, PCH), 6.85 (s, 1 H, H-4, imidazolyl), 6.92 (dd, $^3J_{HH}$ = 5.3 Hz, $^3J_{HP}$ = 15.2 Hz, 1 H, OH), 6.92 (m, 7 H, 4 H_m, 2 H_p, C_6H_5 + 1 H, =CH), 7.62 (s, 1 H, H-5, imidazolyl), 7.86, 7.99 (2 dd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HP}$ = 12.1 Hz, H_o, C_6H_5).

^{13}C NMR (100.61 Hz, DMSO-d_6): δ = 69.9 (d, $^1J_{CP}$ = 71.1 Hz, PCH), 101.2 (=CH_2), 117.3 (C-5, imidazolyl), 127.9 (C-4, imidazolyl), 128.3 (2 d, $^3J_{CP}$ = 12.6 Hz, $^3J_{CP}$ = 12.5 Hz, C_m, C_6H_5), 130.4 (CH=), 130.7 (d, $^1J_{CP}$ = 78.9 Hz, C_{ipso}, C_6H_5), 131.7 (d, $^4J_{CP}$ = 8.2 Hz, C_p, C_6H_5), 131.8 (d, $^2J_{CP}$ = 9.9 Hz, C_o, C_6H_5), 131.9 (d, $^1J_{CP}$ = 78.9 Hz, C_{ipso}, C_6H_5), 132.7 (d, $^2J_{CP}$ = 9.9 Hz, C_o, C_6H_5), 142.9 (C-2, imidazolyl).

^{15}N NMR (40.56 MHz, $CDCl_3$): δ = –194.1 (N-1), –118.0 (N-3).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 47.0.

Anal. Calcd for $C_{18}H_{17}N_2OPS$: C, 63.52; H, 5.03; N, 8.23; P, 9.10; S, 9.42. Found: C, 63.51; H, 5.02; N, 8.23; P, 9.07; S, 9.39.

(Diphenylphosphorothioyl)(1-vinyl-1*H*-benzimidazol-2-yl)methanol (18g)

Prepared from **13** (218 mg, 1 mmol) and **11** (172 mg, 1 mmol); yield: 374 mg (96%); yellow powder; mp 167–168 °C (hexane).

IR (KBr): 3167 (OH), 614 cm^{-1} (P=S).

^{1}H NMR (400.13 MHz, DMSO-d_6): δ = 5.16 (d, $^3J_{HH}$ = 9.2 Hz, 1 H, =CH_2), 5.52 (d, $^3J_{HH}$ = 16.0 Hz, 1 H, =CH_2), 6.29 (dd, $^3J_{HH}$ = 6.1 Hz, $^2J_{HP}$ = 7.6 Hz, 1 H, PCH), 7.16 (dd, $^3J_{HH}$ = 6.1 Hz, $^3J_{HP}$ = 14.0 Hz, 1 H, OH), 7.24 (dd, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 8.8 Hz, 1 H_{arom}, H-5), 7.30 (dd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 8.8 Hz, 1 H_{arom}, H-6), 7.51–7.62 (m, 8 H, 4 H_m, 2 H_p, C_6H_5, 1 H_{arom}, H-4, + 1 H, =CH), 7.72 (d, $^3J_{HH}$ = 7.9 Hz, 1 H_{arom}, H-7), 7.95, 8.02 (2 ddd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HP}$ = 11.9 Hz, 4 H, H_o, C_6H_5).

^{13}C NMR (100.61 Hz, DMSO-d_6): δ = 70.7 (d, $^1J_{CP}$ = 69.8 Hz, PCH), 107.2 (=CH_2), 112.4 (C-7, Ar), 119.9 (C-4, Ar), 123.2 (C-5, Ar), 124.1 (C-6, Ar), 128.5 (d, $^3J_{CP}$ = 12.1 Hz, C_m, C_6H_5), 128.9 (d, $^3J_{CP}$ = 11.6 Hz, C_m, C_6H_5), 129.9 (d, $^1J_{CP}$ = 78.0 Hz, C_{ipso}, C_6H_5), 130.4 (CH=), 132.0 (d, $^2J_{CP}$ = 9.9 Hz, C_o, C_6H_5), 132.2 (d, $^4J_{CP}$ = 2.2 Hz, C_p, C_6H_5), 132.25 (d, $^4J_{CP}$ = 2.6 Hz, C_p, C_6H_5), 132.3 (d, $^1J_{CP}$ = 78.4 Hz, C_{ipso}, C_6H_5), 133.3 (d, $^2J_{CP}$ = 9.9 Hz, C_o, C_6H_5), 133.7 (C-9, Ar), 142.6 (C-8, Ar), 150.2 (C-2, Ar).

^{15}N NMR (40.56 MHz, DMSO-d_6): δ = –214.4 (N-1), –129.2 (N-3).

^{31}P NMR (161.98 MHz, DMSO-d_6): δ = 46.4.

Anal. Calcd for $C_{22}H_{19}N_2OPS$: C, 67.68; H, 4.90; N, 7.17; P, 7.93; S, 8.21. Found: C, 67.65; H, 4.90; N, 7.15; P, 7.89; S, 8.19.

[Bis(2-pyridin-2-ylethyl)phosphorothioyl](phenyl)methanol (18h)

Prepared from **14** (276 mg, 1 mmol) and **5** (106 mg, 1 mmol); yield: 371 mg (97%); white powder; mp 110–111 °C (hexane).

IR (KBr): 3200 (OH), 614 cm^{-1} (P=S).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 2.09–2.27, 2.60–2.68, 2.69–2.77 (m, 4 H, PyCH_2), 2.89–2.99, 3.13–3.24, 3.26–3.37 (m, 4 H, CH_2P), 4.03 (br s, 1 H, OH), 5.05 (s, 1 H, PCH), 7.05 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, H-3, Py), 7.10 (dd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 5.3 Hz, 1 H, H-4, Py), 7.18 (dd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 5.3 Hz, 1 H, H-4, Py), 7.24 (d, $^3J_{HH}$ = 7.9 Hz, 1 H, H-3, Py), 7.28–7.35 (m, 3 H, H_m, H_p, C_6H_5CHOH), 7.56 (m, 3 H, 1 H, H-5, Py, 2 H, H_o, C_6H_5CHOH), 7.66 (dd, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 7.6 Hz, 1 H, H-5, Py), 8.47 (m, 2 H, H-6, Py).

^{13}C NMR (100.61 Hz, $CDCl_3$): δ = 24.8 (d, $^1J_{CP}$ = 47.0 Hz, CH_2P), 25.9 (d, $^1J_{CP}$ = 47.0 Hz, CH_2P), 29.0 (PyCH_2), 29.8 (d, $^1J_{CP}$ = 2.6 Hz, PyCH_2), 73.3 (d, $^1J_{CP}$ = 56.5 Hz, PCH), 121.0, 121.3 (C-5, Py), 122.1, 122.4 (C-3, Py), 126.6 (d, $^3J_{CP}$ = 3.4 Hz, C_o, C_6H_5CHOH), 127.3 (d, $^4J_{CP}$ = 2.6 Hz, C_m, C_6H_5CHOH), 127.4 (d, $^3J_{CP}$ = 3.0 Hz, C_p, C_6H_5CHOH), 135.6 (C_{ipso}, C_6H_5CHOH), 136.1, 136.6 (C-4, Py), 148.0, 148.6 (C-6, Py), 159.6 (d, $^3J_{CP}$ = 10.8 Hz, C-2, Py), 159.8 (d, $^3J_{CP}$ = 14.2 Hz, C-2, Py).

^{15}N NMR (40.56 MHz, $CDCl_3$): δ = –65.9.

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 61.0.

Anal. Calcd for $C_{21}H_{23}N_2OPS$: C, 65.95; H, 6.06; N, 7.32; P, 8.10; S, 8.38. Found: C, 65.91; H, 6.05; N, 7.31; P, 8.07; S, 8.37.

[Bis(2-pyridin-2-ylethyl)phosphorothioyl](2-furyl)methanol (18i)

Prepared from **14** (276 mg, 1 mmol) and **6** (96 mg, 1 mmol); yield: 361 mg (97%); yellow powder; mp 94–95 °C (hexane).

IR (KBr): 3143 (OH), 613 cm^{-1} (P=S).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 2.17–2.23, 2.45–2.47, 2.60–2.66 (m, 4 H, PyCH_2), 3.02–3.15, 3.26–3.30 (m, 4 H, CH_2P), 5.03 (d, $^2J_{HP}$ = 1.8 Hz, 1 H, PCH), 6.36 (dd, $^3J_{HH}$ = 3.1 Hz, $^3J_{HH}$ = 2.0 Hz, 1 H, H-4, furyl), 6.47 (dd, $^3J_{HH}$ = 3.9 Hz, $^3J_{HH}$ = 3.1 Hz, 1 H, H-3, furyl), 6.80 (br s, 1 H, OH), 7.09, 7.14 (2 dd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 4.6 Hz, 1 H, H-5, Py), 7.20, 7.18 (2 d, $^3J_{HH}$ = 8.0 Hz, 2 H, H-3, Py), 7.39 (d, $^3J_{HH}$ = 2.0 Hz, 1 H, H-5, furyl), 7.57, 7.51 (2 dd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 8.0 Hz, 2 H, 4-H, Py), 8.43, 8.47 (2 dd, $^3J_{HH}$ = 2 H, H-6, Py).

^{13}C NMR (100.61 Hz, $CDCl_3$): δ = 26.4, 27.1 (2 d, $^1J_{PC}$ = 47.0 Hz, CH_2P), 29.3, 30.3 (PyCH_2), 69.0 (d, $^1J_{PC}$ = 58.2 Hz, PCH), 109.5 (d, $^3J_{CP}$ = 6.0 Hz, C-3, furyl), 110.8 (C-4, furyl), 121.6, 121.8 (C-5, Py), 123.1, 123.6 (C-3, Py), 136.7, 137.2 (C-4, Py), 142.8 (d, $^1J_{CP}$ = 2.2 Hz, C-5, furyl), 148.6, 149.1 (C-6, Py), 149.4 (C-2, furyl), 159.9 ($^3J_{CP}$ = 9.5 Hz, C-2, Py), 160.2 ($^3J_{CP}$ =13.8 Hz, C-2, Py).

^{15}N NMR (40.56 MHz, $CDCl_3$): δ = –72.6, –81.2.

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 60.5.

Anal. Calcd for $C_{19}H_{21}N_2O_2PS$: C, 61.28; H, 5.68; N, 7.52; P, 8.32; S, 8.61. Found: C, 61.26; H, 5.68; N, 7.51; P, 8.28; S, 8.60.

(2*E*)-1-[Bis(2-phenylethyl)phosphoroselenoyl]-3-phenylprop-2-en-1-ol (18j)

Prepared from **15** (321 mg, 1 mmol) and **4** (132 mg, 1 mmol); yield: 435 mg (96%); yellow powder; mp 116–117 °C (hexane).

IR (KBr): 3343 (OH), 440 cm^{-1} (P=Se).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 2.10–2.18, 2.22–2.38 (m, 4 H, CH_2P), 2.90–3.05 (m, 4 H, PhCH_2), 3.14 (br s, 1 H, OH), 4.49 (dd, $^3J_{HH}$ = 6.8 Hz, $^2J_{HP}$ = 1.5 Hz, 1 H, PCH), 6.25, 6.28 (2 dd, $^3J_{HH}$ = 15.9 Hz, $^3J_{HH}$ = 6.8 Hz, $^3J_{HP}$ = 4.5 Hz, 1 H, =CH), 6.70, 6.74 (2 d, $^3J_{HH}$ = 15.9 Hz, $^4J_{HP}$ = 3.8 Hz, 1 H, =C*H*Ph), 7.14–7.38 (m, 15 H, 3 × C_6H_5).

^{13}C NMR (100.61 Hz, $CDCl_3$): δ = 28.9 (d, $^1J_{PC}$ = 37.6 Hz, CH_2P), 29.3 (d, $^1J_{PC}$ = 37.9 Hz, CH_2P), 29.28, 29.4 (2 d, $^2J_{CP}$ = 2.5 Hz, $PhCH_2$), 71.5 (d, $^1J_{CP}$ = 47.6 Hz, PCH), 122.7 (d, $^2J_{CP}$ = 3.0 Hz, PCHC=), 126.6 (C_m, C_6H_5C=), 126.7 (C_o, C_6H_5C=), 128.3, 128.4 (C_o, $C_6H_5CH_2$), 128.5 (C_p, C_6H_5C=), 128.7 (C_p, $C_6H_5CH_2$), 128.8 (C_m, $C_6H_5CH_2$), 133.6 (d, $^4J_{CP}$ = 2.9 Hz, C_{ipso}, C_6H_5C=), 133.8 (d, $^3J_{CP}$ = 11.2 Hz, PhC=), 140.3 (d, $^3J_{CP}$ = 11.0 Hz, C_{ipso}, $C_6H_5CH_2$), 140.5 (d, $^3J_{CP}$ = 11.8 Hz, C_{ipso}, $C_6H_5CH_2$).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 51.6 (s), (+d satellite, $^1J_{PSe}$ = 697.1 Hz).

^{77}Se NMR (161.98 MHz, $CDCl_3$): δ = –450.3 ($^1J_{SeP}$ = 697.1 Hz).

Anal. Calcd for $C_{25}H_{27}OPSe$: C, 66.22; H, 6.00; P, 6.83; Se, 17.41. Found: C, 66.19; H, 6.01; P, 6.79; Se, 17.39.

[Bis(2-phenylethyl)phosphoroselenoyl](phenyl)methanol (18k)

Prepared from **15** (321 mg, 1 mmol) and **5** (106 mg, 1 mmol); yield: 414 mg (97%); white powder; mp 88–89 °C (hexane).

IR (KBr): 3297 (OH), 458 cm^{-1} (P=Se).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.75–1.86, 1.93–2.03, 2.11–2.31 (m, 4 H, CH_2P), 2.55–2.75, 2.91–2.98 (m, 4 H, $PhCH_2$), 3.82 (br s, 1 H, OH), 4.88 (s, 1 H, PCH), 6.99 (d, $^3J_{HH}$ = 7.6 Hz, 2 H, H_o, C_6H_5CHOH), 7.14–7.23 (m, 4 H, H_m, $C_6H_5CH_2$, 2 H, H_p, $C_6H_5CH_2$), 7.28 (dd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 7.6 Hz, 2 H, H_m, C_6H_5CHOH), 7.33–7.40 (m, 4 H, $C_6H_5CH_2$, 1 H, H_p, C_6H_5CHOH).

^{13}C NMR (100.61 Hz, $CDCl_3$): δ = 28.6 (d, $^1J_{CP}$ = 37.1 Hz, CH_2P), 29.4 (d, $^2J_{CP}$ = 2.6 Hz, $PhCH_2$), 29.6 (d, $^2J_{CP}$ = 2.6 Hz, $PhCH_2$), 30.0 (d, $^1J_{CP}$ = 37.5 Hz, CH_2P), 71.9 (d, $^1J_{CP}$ = 42.7 Hz, PCH), 126.6 (C_p, $C_6H_5CH_2$), 126.7 (d, $^3J_{CP}$ = 4.7 Hz, C_o, C_6H_5CHOH), 126.8 (C_p, $C_6H_5CH_2$), 128.3, 128.4 (C_m, $C_6H_5CH_2$), 128.7 (C_o, $C_6H_5CH_2$), 128.8 (d, $^4J_{CP}$ = 2.6 Hz, C_m, C_6H_5CHOH), 128.83 (C_o, $C_6H_5CH_2$), 129.0 (d, $^5J_{CP}$ = 3.0 Hz, C_p, C_6H_5CHOH), 135.8 (d, $^2J_{CP}$ = 2.2 Hz, C_{ipso}, C_6H_5CHOH), 140.3 (d, $^3J_{CP}$ = 13.8 Hz), 140.5 (d, $^3J_{CP}$ = 14.7 Hz, C_{ipso}, $C_6H_5CH_2$).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 54.5 (s) (+d satellite, $^1J_{PSe}$ = 696.0 Hz).

^{77}Se NMR (161.98 MHz, $CDCl_3$): δ = –461.3 ($^1J_{SeP}$ = 696.0 Hz).

Anal. Calcd for $C_{23}H_{25}OPSe$: C, 64.64; H, 5.90; P, 7.25; Se, 18.48. Found: C, 64.60; H, 5.89; P, 7.22; Se, 18.46.

[Bis(2-phenylethyl)phosphoroselenoyl](2-furyl)methanol (18l)

Prepared from **15** (321 mg, 1 mmol) and **6** (96 mg, 1 mmol); yield: 404 mg (97%); white powder; mp 76–77 °C (hexane).

IR (KBr): 3203 (OH), 484 cm^{-1} (P=Se).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.89–1.99, 2.05–2.15, 2.19–2.39 (m, 4 H, CH_2P), 2.71–2.80, 2.92–2.99 (m, 4 H, $PhCH_2$), 3.65 (br s, 1 H, OH), 4.91 (s, 1 H, PCH), 6.41 (dd, $^3J_{HH}$ = 3.3 Hz, $^3J_{HH}$ = 1.8 Hz, 1 H, H-4, furyl), 6.48 (dd, $^3J_{HP}$ = 3.9 Hz, $^3J_{HH}$ = 3.3 Hz, 1 H, H-3, furyl), 7.07 (d, $^3J_{HH}$ = 7.7 Hz, 2 H, H_o, C_6H_5), 7.15–7.30 (m, 2 H, H_o, 4 H, H_m, 2 H, H_p, C_6H_5), 7.43 (dd, $^3J_{HH}$ = 1.8 Hz, $^5J_{PH}$ = 2.9 Hz, 1 H, H-5, furyl).

^{13}C NMR (100.61 Hz, $CDCl_3$): δ = 29.26, 29.3 (2 d, $^2J_{PC}$ = 2.6 Hz, $PhCH_2$), 29.4 (d, $^1J_{PC}$ = 37.1 Hz, CH_2P), 30.3 (d, $^1J_{PC}$ = 37.9 Hz, CH_2P), 66.5 (d, $^1J_{PC}$ = 46.1 Hz, PCH), 109.4 (d, $^3J_{CP}$ = 6.0 Hz, C-3, furyl), 111.2 (d, $^4J_{CP}$ = 2.2 Hz, C-4, furyl), 126.7, 126.8 (C_p, C_6H_5) 128.4, 128.5 (C_o, C_6H_5) 128.8, 128.9 (C_m, C_6H_5), 140.4 (d, $^3J_{CP}$ = 14.2 Hz, C_{ipso}, C_6H_5), 140.6 (d, $^3J_{CP}$ = 15.5 Hz, C_{ipso}, C_6H_5), 143.0 (d, $^1J_{CP}$ = 3.0 Hz, C-5, furyl), 143.1 (d, $^1J_{CP}$ = 3.0 Hz, C-2, furyl).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 53.6 (s) (+d satellite, $^1J_{PSe}$ = 697.9 Hz).

^{77}Se NMR (161.98 MHz, $CDCl_3$): δ = –459.8 ($^1J_{SeP}$ = 697.9 Hz).

Anal. Calcd for $C_{21}H_{23}O_2PSe$: C, 60.44; H, 5.55; P, 7.42; Se, 18.92. Found: C, 60.41; H, 5.52; P, 7.39; Se, 18.90.

(Diphenylphosphoroselenoyl)(phenyl)methanol (18m)

Prepared from **16** (266 mg, 1 mmol) and **5** (106 mg, 1 mmol); yield: 365 mg (98%); white powder; mp 129–130 °C (hexane).

IR (KBr): 3256 (OH), 492 cm^{-1} (P=Se).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 3.91 (br s, 1 H, OH), 5.53 (s, 1 H, PCH), 6.98 (d, $^3J_{HH}$ = 7.6 Hz, 2 H, H_o, C_6H_5CHOH), 7.08 (dd, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 7.6 Hz, 2 H, H_m, C_6H_5CHOH), 7.15 (t, $^3J_{HH}$ = 7.6 Hz, 1 H, H_p, C_6H_5CHOH), 7.20–7.25 (m, 2 H, H_m, C_6H_5P), 7.35–7.39 (m, 1 H, H_p, C_6H_5P), 7.41–7.47 (m, 2 H, H_o, C_6H_5P, 2 H, H_m, C_6H_5P), 7.49–7.52 (m, 2 H, H_p, C_6H_5P), 7.87 (dd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 12.2 Hz, 2 H, H_o, C_6H_5P).

^{13}C NMR (100.61 Hz, $CDCl_3$): δ = 72.5 (d, $^1J_{CP}$ = 46.5 Hz, PCH), 127.5 (d, $^3J_{CP}$ = 4.7 Hz, C_o, C_6H_5CHOH), 127.6 (d, $^4J_{CP}$ = 2.6 Hz, C_m, C_6H_5CHOH), 128.2 (d, $^3J_{CP}$ = 12.1 Hz, C_m, C_6H_5P), 128.4 (d, $^5J_{CP}$ = 3.0 Hz, C_p, C_6H_5CHOH), 128.8 (d, $^3J_{CP}$ = 11.6 Hz, C_m, C_6H_5P), 129.8 (d, $^1J_{CP}$ = 68.5 Hz, C_{ipso}, C_6H_5P), 132.0 (d, $^2J_{CP}$ = 3.5 Hz, C_p, C_6H_5P), 132.1 (d, $^2J_{CP}$ = 3.5 Hz, C_p, C_6H_5P), 135.5 (C_{ipso}, C_6H_5CHOH).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 51.1 (s) (+d satellite, $^1J_{PSe}$ = 713.2 Hz).

^{77}Se NMR (161.98 MHz, $CDCl_3$): δ = –380.0 ($^1J_{SeP}$ = 713.2 Hz).

Anal. Calcd for $C_{19}H_{17}OPSe$: C, 61.47; H, 4.62; P, 8.34; Se, 21.27. Found: C, 61.45; H, 4.62; P, 8.31; Se, 21.28.

Reaction of α-Hydroxyphosphine Oxide 12d with Methyl Propiolate

A solution of α-hydroxyphosphine oxide **12d** (365 mg, 1.0 mmol), methyl propiolate (92 mg, 1.1 mmol), and Et_3N (101 mg, 1 mmol) in THF (4 mL) was stirred at 20–22 °C for 5 h. The solvent was removed under reduced pressure. The residue was washed with hexane (2 × 0.5 mL) and dried under vacuum to afford methyl (*E*)-3-[(diphenethylphosphoryl)(2-pyridinyl)methoxy]prop-2-enoate (**19**); yield: 395 mg (88%); white powder; mp 96–97 °C (hexane).

IR (KBr): 1716 (C=O), 1641, 1627 (C=C of vinyl), 1157 cm^{-1} (P=O).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ = 1.95–2.79 (m, 4 H, CH_2P), 2.74–2.98 (m, 4 H, $PhCH_2$), 3.64 (3 H, CH_3), 5.27 (d, $^3J_{HH}$ = 12.6 Hz, 1 H, =CH), 5.29 (d, $^3J_{HH}$ = 7.8 Hz, 1 H, PCH), 7.14–7.21 (m, 6 H, H_p, H_m, C_6H_5), 7.24–7.29 (m, 5 H, 4 H_o, C_6H_5 + H-4, Py), 7.45 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, H-6, Py), 7.50 (d, $^3J_{HH}$ = 12.6 Hz, 1 H, OCH=), 7.74 (dd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 8.4 Hz, 1 H, H-5, Py), 8.62 ($^3J_{HH}$ = 4.6 Hz, H-3, Py).

^{13}C NMR (100.61 Hz, $CDCl_3$): δ = 26.9, 27.0 (2 d, $^2J_{CP}$ = 3.6 Hz, $PhCH_2$), 27.5 (d, $^1J_{CP}$ = 62.0 Hz, CH_2P), 27.6 (d, $^1J_{CP}$ = 61.2 Hz, CH_2P), 50.9 (CH_3), 81.1 (d, $^1J_{CP}$ = 72.0 Hz, PCH), 99.8 (=CH), 122.3 (d, $^3J_{CP}$ = 2.6 Hz, C-6, Py), 123.4 (C-4, Py), 126.15, 126.2 (C_p, C_6H_5), 127.7, 127.8 (C_o, C_6H_5), 128.3, 128.4 (C_m, C_6H_5), 136.9 (C-5, Py), 140.2, 140.3 (2 d, $^3J_{CP}$ = 10.8 Hz, C_{ipso}, C_6H_5), 149.4 (C-3, Py), 152.5 (C-1, Py), 160.4 (d, $^1J_{CP}$ = 9.9 Hz, OCH=), 166.7 (C=O).

^{15}N NMR (40.56 MHz, $CDCl_3$): δ = –68.8 (d, $^2J_{NH}$ = 14.6 Hz).

^{31}P NMR (161.98 MHz, $CDCl_3$): δ = 43.5.

Anal. Calcd for $C_{26}H_{28}NO_4P$: C, 69.48; H, 6.28; N, 3.12; P, 6.89. Found: C, 69.44; H, 6.23; N, 3.09; P, 6.85.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0034-1380408.

References

(1) (a) Gusarova, N. K.; Reutskaya, A. M.; Ivanova, N. I.; Medvedeva, A. S.; Demina, M. M.; Novopashin, P. S.; Afonin, A. V.; Albanov, A. I.; Trofimov, B. A. *J. Organomet. Chem.* **2002**, *659*, 172. (b) Gusarova, N. K.; Arbuzova, S. N.; Reutskaya, A. M.; Ivanova, N. I.; Baikalova, L. V.; Sinegovskaya, L. M.; Chipanina, N. N.; Afonin, A. V.; Zyryanova, I. A. *Chem. Heterocycl. Compd.* **2002**, *38*, 65. (c) Ivanova, N. I.; Reutskaya, A. M.; Gusarova, N. K.; Medvedeva, S. A.; Afonin, A. V.; Ushakov, I. A.; Tatarinova, A. A.; Trofimov, B. A. *Russ. J. Gen. Chem.* **2003**, *73*, 1354. (d) Ivanova, N. I.; Gusarova, N. K.; Nikitina, E. A.; Albanov, A. I.; Sinegovskaya, L. M.; Nikitin, M. V.; Konovalova, N. A.; Trofimov, B. A. *Phosphorus, Sulfur Silicon Relat. Elem.* **2004**, *179*, 7. (e) Ivanova, N. I.; Gusarova, N. K.; Nikitina, E. A.; Medvedeva, S. A.; Al'pert, M. L.; Trofimov, B. A. *Chem. Heterocycl. Compd.* **2004**, *40*, 426. (f) Priya, S.; Balakrishna, M. S.; Mobin, S. M. *Polyhedron* **2005**, *24*, 1641. (g) Liu, W.-Y.; Huo, P.; Gao, Y.-X.; Liu, P.; Zhao, Y.-F. *Acta Crystallogr., Sect. E* **2007**, *63*, 1008. (h) Liu, W.-Y.; Huo, P. *Acta Crystallogr., Sect. E* **2008**, *64*, 233. (i) Yuan, X.-L.; Liu, W.-Y.; Huo, P.; Mei, G.-O. *Acta Crystallogr., Sect. E* **2010**, *66*, 2331. (j) Keglevich, G.; To'th, V. R.; Drahos, L. *Heteroat. Chem.* **2011**, *22*, 15. (k) Ivanova, N. I.; Volkov, P. A.; Gusarova, N. K.; Larina, L. I.; Trofimov, B. A. *Russ. J. Gen. Chem.* **2011**, *81*, 315. (l) Luo, X.; Zhou, Z.; Li, X.; Liang, X.; Ye, J. *RSC Adv.* **2011**, *1*, 698. (m) Zheng, J.; Feng, X.; Yu, Y.; Zhen, X.; Zhao, Y. *Phosphorus, Sulfur Silicon Relat. Elem.* **2013**, *188*, 1080. (n) Kortmann, F. A.; Chang, M.-C.; Otten, E.; Couzijn, E. P. A.; Lutz, M.; Minnaard, A. J. *Chem. Sci.* **2014**, *5*, 1322.

(2) (a) Trofimov, B. A.; Gusarova, N. K.; Ivanova, N. I.; Konovalova, N. A.; Bogdanova, M. V.; Albanov, A. I.; Avseenko, N. D.; Sukhov, B. G. *Russ. J. Gen. Chem.* **2004**, *74*, 1625. (b) Ivanova, N. I.; Baikalova, L. V.; Konovalova, N. A.; Zyryanova, I. A.; Albanov, A. I.; Sinegovskaya, L. M.; Kukhareva, V. A.; Tatarinova, A. A.; Avseenko, N. D.; Sukhov, B. G.; Gusarova, N. K.; Trofimov, B. A. *Chem. Heterocycl. Compd.* **2005**, *41*, 317. (c) Ivanova, N. I.; Volkov, P. A.; Baikalova, L. V.; Gusarova, N. K.; Trofimov, B. A. *Chem. Heterocycl. Compd.* **2008**, *44*, 1359.

(3) Gusarova, N. K.; Ivanova, N. I.; Konovalova, N. A.; Sukhov, B. G.; Baikalova, L. V.; Sinegovskaya, L. M.; Pavlov, D. V.; Trofimov, B. A. *Synthesis* **2006**, 4159.

(4) Clark, H. J.; Wang, R.; Alper, H. *J. Org. Chem.* **2002**, *67*, 6224.

(5) Chen, M. J.; Chen, C. R.; Tan, Y.; Huang, J. Q.; Wang, X. L.; Chen, L.; Wang, Y. Z. *Ind. Eng. Chem. Res.* **2014**, *53*, 1160.

(6) Moiseev, D. V.; James, B. R.; Hu, T. Q. *Phosphorus, Sulfur Silicon Relat. Elem.* **2012**, *187*, 433.

(7) (a) Cristau, H. J.; Brahic, C.; Pirat, J. L. *Tetrahedron* **2001**, *57*, 9149. (b) Nawrot, B.; Michalak, O.; Clercq, E. D.; Stec, W. J. *Antivir. Chem. Chemother.* **2004**, *15*, 319.

(8) (a) Trofimov, B. A.; Gusarova, N. K. *Mendeleev Commun.* **2009**, *19*, 295. (b) Gusarova, N. K.; Arbuzova, S. N.; Trofimov, B. A. *Pure Appl. Chem.* **2012**, *84*, 439.

(9) Well, M.; Schmutzler, R. *Phosphorus, Sulfur Silicon Relat. Elem.* **1992**, *72*, 171.

(10) (a) Afonin, A. V.; Baikalova, L. V.; Domnina, E. S. *Russ. Chem. Bull.* **1996**, *45*, 1137. (b) Baikalova, L. V.; Domnina, E. S.; Chipanina, N. N.; Afonin, A. V.; Shulunova, A. M. *Russ. Chem. Bull.* **1999**, *48*, 962.

(11) (a) Peters, G. *J. Am. Chem. Soc.* **1960**, *82*, 4751. (b) Maier, L. *Helv. Chim. Acta* **1966**, *49*, 1000.

(12) Bodenhausen, G.; Ruben, D. *J. Chem. Phys. Lett.* **1980**, *69*, 185.

(13) Bax, A.; Summers, M. F. *J. Am. Chem. Soc.* **1986**, *108*, 2093.

(14) CCDC 1038369–1038371 contain the supplementary crystallographic data of compounds **12l**, **18d**, and **18m**, respectively. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44(1223)336033; E-mail: deposit@ccdc.cam.ac.uk.

(15) Sheldrick, G. M. *Acta Crystallogr., Sect. D* **2008**, *64*, 112.

(16) Emoto, T.; Gomi, H.; Yoshifuji, M.; Okazaki, R.; Inamoto, N. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 2449.