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# Reactions of Nitroxides, Part XI: *O*-Aryl Phenylselenophosphonates Bearing a Nitroxyl Moiety

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ABSTRACT: *O-Aryl phenylselenophosphonates bearing a nitroxyl moiety were synthesized in the presence of pyridine in diethyl ether from 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl, and either phenyldichlorophosphine and elemental selenium in 9–35% yield or phenyldichlorophosphine selenide in 36–62% yield. O,O-Diaryl phenylselenophosphonates and O,O-bis(2,2,6,6-tetramethyl-1-oxyl-4-piperidyl)phenylselenophosphonates were obtained as by-products. O,O-Diaryl phenylselenophosphonates were obtained from phenyldichlorophosphine selenide and 2 mol of phenols in 55–86% yield. Antifungal activity of some synthesized selenophosphonates was found.* © 2011 Wiley Periodicals, Inc. Heteroatom Chem 22:137–147, 2011; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.20667

## *INTRODUCTION*

Selenium plays an important role in living organisms (for some recent reviews, see [2–10]). This element is found in plants mostly as selenomethionine ($CH_3SeCH_2CH_2CH(NH_2)COOH$) [10]. In animals, all essential functions of selenium have been associated with selenoproteins, which contain selenocysteine ($HSeCH_2CH(NH_2)COOH$) as a part of an active site [7,10]. The important relation of selenium-containing compounds to cancer is discussed [3,5–7,11].

The role of selenium in agriculture has been recently reviewed [10]. This role is controversial. The hyperaccumulation of selenium in plants can cause selenosis in animals [2]. The toxicity of selenophosphates to mice was also investigated [12]. In spite of that, attempts to apply selenium-containing compounds as insecticides: beta-selenolactams [13] and selenophosphates [12] were described. Recently, we have investigated antifungal properties of the selenoureas bearing a nitroxyl moiety [14]. Because there are only a few examples of nitroxyl radicals containing a selenium atom [15,16] or P=Se moiety [17,18], we are encouraged to continue the investigation of the antifungal properties of the nitroxyl radicals with a P=Se function. Herein, we present the synthesis and antifungal evaluation of phenylselenophosphonates bearing a nitroxyl moiety.

## *RESULTS AND DISCUSSION*

Synthesis of phenylselenophosphonates bearing a nitroxyl moiety is shown in Scheme 1.

Phenyldichlorophosphine selenide [**1b**, $PhP(=Se)Cl_2$] was obtained by direct selenization of phenyldichlorophosphine (**1a**) at 175–180°C for 1.5 h in 59.7% yield (double distillation) [19,20].

As selenization of trivalent phosphorus is a typical method of building the P=Se bond, phosphorylation of 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl

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For Part X, see [1].

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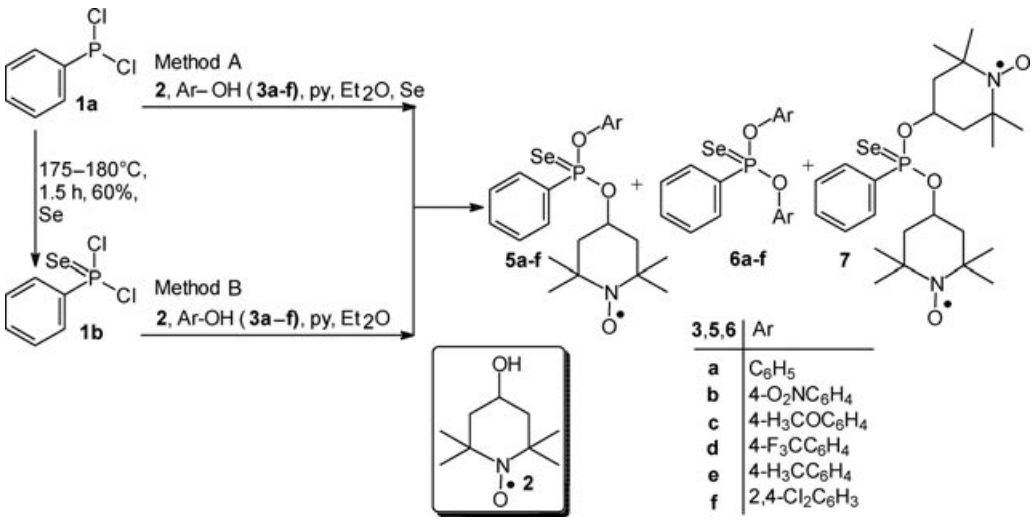



**SCHEME 1** Synthesis of phenylselenophosphonates bearing a nitroxyl moiety.

(TEMPOL, **2**) and phenols **3a–f** was achieved with phenyldichlorophosphine (**1a**) and black selenium in diethyl ether in the presence of pyridine (method A). Alternatively, TEMPOL (**2**) and phenols **3a–f** were phosphorylated with phenyldichlorophosphine selenide (**1b**) (method B). The *O*-aryl phenylselenophosphonates bearing a nitroxyl moiety **5a–f**, diaryl esters **6a–f**, and dinitroxyl diradical **7** were the products in both cases (Scheme 1 and Table 1). As shown in Table 1, when phenyldichlorophosphine selenide (**1b**) was used as a starting compound (method B), the target nitroxides **5a–f** were obtained in higher yields.

Phenylselenophosphonic 2,2,6,6-tetramethyl-1-oxyl-4-oxypiperidyl chloride (**4**) was obtained from phenyldichlorophosphine selenide (**1b**) and TEMPOL (**2**) in the presence of pyridine in diethyl ether in 35.4% yield (mp 42–52°C).

In the reaction of **1a**, Se (or **1b** instead), phenols **3a–f**, and TEMPOL (**2**), diaryl esters **6a–f** were formed as minor products (see above). To obtain larger amounts of **6a–f** and to evaluate their biological properties, they were prepared via the direct reaction of phenyldichlorophosphine selenide (**1b**) with 2 mol of phenols **3a–f** (Scheme 2 and Table 2).

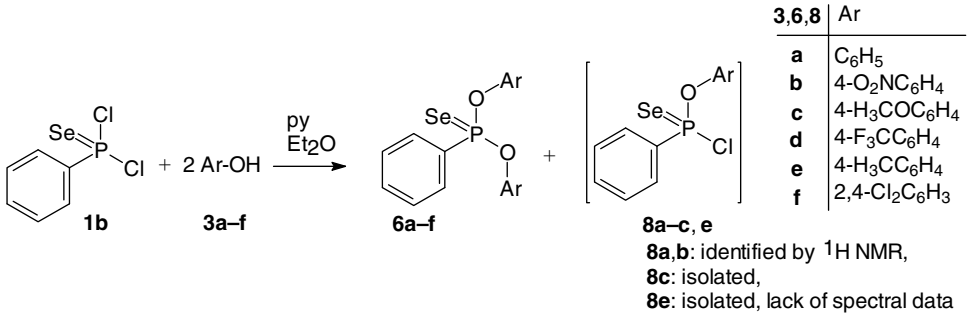
Monochlorides **8c** and **8e** were isolated as side products. **8e** was unstable, and the confirmation of its structure was not possible. The presence of monochlorides **8a** and **8b** was proved from $^1$H NMR spectra.

It is worthy to note that the attempts to react both monochloride **4** with an equivalent amount of phenol **3a** to get **5a** and monochloride **8c** with an equivalent of 4-methoxyphenol **3c** to get the diester **6c**, were unsuccessful (Scheme 3). Unreacted starting **4** or **8c** remained unchanged (TLC).

**TABLE 1** Products **5a–f**/**6a–f**/**7** in the Reaction of a Phenol + TEMPOL (**2**) + $PhPCl_2$ (**1a**) + Se (Method A) versus the Reaction of a Phenol + TEMPOL (**2**) + $PhP(=Se)Cl_2$ (**1b**) (Method B)

| | *Phenol **3a–f*** | ***5a–f** Method A (%)/meth B (%)* | ***6a–f** Method A (%)/method B (%)* | ***7**[a] Method A (%)/method B (%)* |
|---|---|---|---|---|
| **a** | $C_6H_5OH$ | 35.5/51.2 | 8.6/19.7 | 33.4/14.4 |
| **b** | 4-$O_2NC_6H_4OH$ | 9.1/35.9 | —/7.4 | 34.1/8.0 |
| **c** | 4-$CH_3OC_6H_4OH$ | 10.6/56.8[b] | 2.2/9.2 | 34.1/24.6 |
| **d** | 4-$CF_3C_6H_4OH$ | 16.8/48.4 | —/38.1[c] | 11.6/— |
| **e** | 4-$CH_3C_6H_4OH$ | 22.4/61.8 | 30.0/13.2 | 17.7/28.1 |
| **f** | 2,4-di-$Cl_2C_6H_3OH$ | 33.5/59.5 | —/20.6 | 58.7/23.1 |

[a]mp: 85–89°C (110–116°C [17]).
[b]mp: 71–75°C.
[c]mp: 41–46°C.




**SCHEME 2** Synthesis of diaryl phenylselenophosphonates **6a–f**.

The reaction of TEMPOL (**2**), and either **1a** and selenium (method A) or **1b** (method B), was repeated with alcohols (cyclohexanol, cyclopentanol, benzyl alcohol, *n*-hexanol, *tert*-butanol, and isopropanol). Analogous phenylselenophosphonates **5** and appropriate diaryl esters **6** were obtained; however, the products were strongly contaminated with phenylselenophosphonic monochlorides **8**. The isolation of pure phenylselenophosphonates **5** and the diaryl esters **6** by flash chromatography was unsuccessful, so the activity of aliphatic nitroxide selenophosphonates and diesters was not tested.

The stability of all synthesized compounds is limited in spite of storage in a refrigerator. Evolution of red selenium is observed sooner or later. Some of the compounds are crystalline; however, their melting points are not sharp. The observed melting point of **7** (85–89°C) is essentially different from the reported literature value (110–116°C [17]).

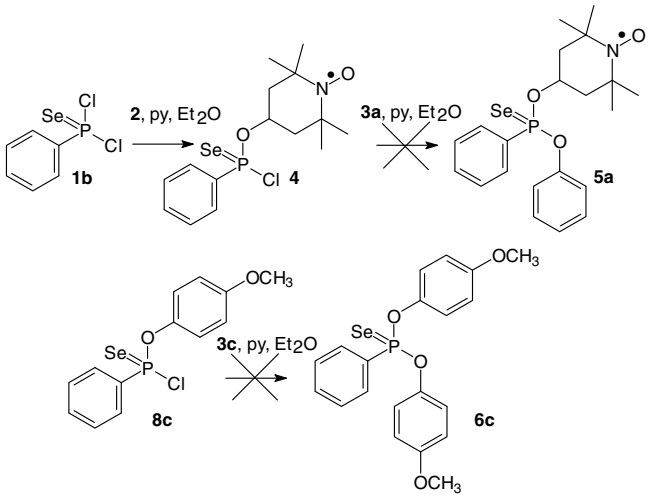
The structures of the synthesized compounds were confirmed by spectroscopic methods. The MS, HR MS, and IR spectra were performed for the compounds bearing a nitroxyl moiety. For the diamagnetic derivatives, the MS, HR MS, IR, $^{1}$H NMR, $^{13}$C NMR, $^{31}$P NMR, and $^{77}$Se NMR spectra were recorded (Tables 3 and 4).

Mass spectra (EI) of nitroxyl esters **5a–f** show characteristic fragmentation ions M-153. In most cases, the abundances of the corresponding M-153 peaks are strong (**5a**: 299 (100), **5b**: 344 (20), **5c**: 329 (84), **5d**: 367 (52), **5e**: 313 (100), **5f**: 367 (8)). More importantly, there are no other fragmentation peaks observed between M and M-153. In Fig. 1, the exemplary mass spectrum of **5e** is presented. Because the M-153 signal shows characteristic selenium pattern, the origin of a M-153 peak should be the elimination of a nitroxyl fragment. In Scheme 4, the elimination of the nitroxyl radical M = 154 is presented. The observed $[M-153]^{+}$ fragment has likely a structure presented in Scheme 4. The proposed structure of $[M-153]^{+}$ fragment was confirmed by HR EI MS analysis (for **5e**): $C_{13}H_{14}O_2P^{80}Se$: calcd: 312.98966, found: 312.98838.

**TABLE 2** Diaryl Phenylselenophoshonates **6a–f** from Phenyldichlorophosphine Selenide (**1b**) and 2 mol of Phenoles **3a–f** (Method B)

| | *Phenol **3a–f*** | ***6a–f** (%)* | ***8** (%)* |
|---|---|---|---|
| **a** | $C_6H_5OH$ | 61.8 | – |
| **b** | 4-$O_2NC_6H_4OH$ | 56.6[a] | – |
| **c** | 4-$CH_3OC_6H_4OH$ | 54.5 | 46.3[b] |
| **d** | 4-$CF_3C_6H_4OH$ | 55.3 | – |
| **e** | 4-$CH_3C_6H_4OH$ | 59.5 | 22.1[c] |
| **f** | 2,4-di-$Cl_2C_6H_3OH$ | 86.3[d] | – |

[a]mp: 50–75°C; decay with selenium evolution.
[b]mp: 45–48°C.
[c]Decomposition with selenium evolution, no spectroscopic data.
[d]mp: 62–71°C.




**SCHEME 3** No products in the reaction of the monochlorides **4** and **8c** with phenols **3a** and **3c**, respectively.

**TABLE 3** MS, HR MS, and IR Data for the Investigated Compounds

| *Compound* | *MS (m/z, int%)* | *HR MS* | *IR ($\nu$, $cm^{-1}$)[b]* |
|---|---|---|---|
| **1b** | EI: 260 (13), 258 (23, M), 256 (9), 223 (7), 178 (31), 159 (17), 157 (20), 143 (100), 107 (37), 77 (42), 51 (30), 50 (14); ESI: [a] 251 (100, $[M + H]^+$), 249 (20), 157 (20) | ESI[a] for $[M + Na]^+$ $C_8H_{11}O_2P^{80}SeNa$ calcd.: 272.9560, found: 272.9555 | Film: 1438, 1096, 745, 712, 683, 619, 589, 517 |
| **4** | EI: 397 (1), 396 (2), 395 (2), 394 (4, M), 393 (1), 392 (2), 243 (8), 242 (3), 241 (14), 240 (6), 239 (7), 238 (5), 237 (4), 225 (2), 223 (2), 221 (3), 205 (3), 203 (1.5), 187 (4), 185 (2), 155 (28), 154 (92), 140 (15), 139 (14), 124 (100), 109 (67), 98 (20) | EI: for M $C_{15}H_{22}NO_2P^{80}SeCl$ calcd.: 394.02419, found: 394.02321. | KBr: 1465, 1439, 1363, 1244, 1179, 1108, 979, 884, 826, 745, 722, 680, 590, 556, 507 |
| **5a** | EI: 453 (4), 452 (8, M), 450 (4), 299 (100), 297 (48), 217 (21), 205 (27), 203 (17), 154 (87), 141 (8), 140 (13), 139 (12), 124 (52), 109 (37), 95 (13), 94 (29), 69 (14), 56 (11), 41 (24) | EI: for M $C_{21}H_{27}NO_3P^{80}Se$ calcd.: 452.08938, found: 452.08781 | Film: 1592, 1488, 1197, 1012, 919, 770, 690, 596, 539 |
| **5b** | EI: 499 (1), 498 (2), 497 (4, M), 496 (1), 495 (2), 344 (20), 342 (11), 326 (4), 262 (9), 205 (15), 203 (10), 154 (100), 140 (10), 139 (10), 124 (69), 109 (38), 69 (18), 56 (19), 55 (32), 41 (27) | EI: for M $C_{21}H_{26}N_2O_5P^{80}Se$ calcd.: 497.07446, found: 497.07564. | Film: 1590, 1524, 1489, 1346, 1216, 1115, 1010, 902, 742, 681, 626, 540 |
| **5c** | EI: 484 (3), 483 (6), 482 (9, M), 480 (6), 331 (19), 330 (14), 329 (84), 328 (10), 327 (56), 326 (21), 325 (18), 311 (19), 247 (12), 231 (7), 205 (15), 189 (11), 188 (9), 187 (7), 186 (6), 185 (4), 154 (100), 140 (27), 125 (14), 124 (76), 123 (43), 109 (48), 100 (6), 98 (9), 95 (11), 83 (8), 82 (6), 81 (13), 77 (12), 74 (12), 69 (20), 67 (15), 58 (14), 56 (15), 55 (39), 41 (42) | EI: for M $C_{22}H_{29}NO_4P^{80}Se$ calcd.: 482.09994, found: 482.09854. | Film: 1503, 1250, 1193, 1116, 1011, 905, 832, 725, 692, 590 |
| **5d** | EI: 520 (8, M), 518 (4), 367 (52), 365 (28), 349 (6), 347 (4), 271 (5), 269 (7), 207 (7), 205 (23), 203 (12), 154 (100), 140 (13), 124 (46), 109 (14), 56 (4), 55 (6), 41 (9) | EI: for M $C_{22}H_{26}F_3NO_3P^{80}Se$ calcd.: 520.07676, found: 520.07785 | Film: 1611, 1511, 1439, 1325, 1214, 1168, 1125, 1067, 1011, 995, 904 |
| **5e** | EI: 467 (4), 466 (12, M), 464 (6), 463 (3), 462 (2), 315 (18), 314 (15), 313 (100), 311 (48), 310 (18), 309 (20), 231 (20), 205 (22), 172 (6), 154 (92), 140 (23), 124 (59), 109 (39), 108 (24), 107 (10), 91 (15) | EI: for M $C_{22}H_{29}NO_3P^{80}Se$ calcd.: 466.10503, found: 466.10317 | Film: 3337, 1615, 1595, 1505, 1460, 1438, 1364, 1198, 1115, 1011, 990, 909, 821, 750, 723, 690, 590, 557, 508 |
| **5f** | EI: 522 (2), 520 (3, M), 518 (2), 396 (2), 394 (3), 392 (2), 369 (13), 367 (8), 365 (8), 287 (4), 285 (6), 241 (11), 205 (7), 154 (95), 140 (40), 124 (100), 109 (47) | EI: for M $C_{21}H_{25}Cl_2NO_3P^{80}Se^{35}$ calcd: 520.01143, found: 520.01396 | Film: 1476, 988, 590, 558, 509 |
| **6a** | EI: 376 (8), 375 (8), 374 (35, M), 372 (18), 371 (7), 299 (3), 297 (3), 281 (12), 279 (6), 217 (100), 203 (22), 201 (14), 77 (29) | EI: for M $C_{18}H_{15}O_2P^{80}Se$ calcd: 373.99749, found: 373.99832 | Film: 1590, 1487, 1185, 917, 771, 688, 595, 528 |
| **6b** | ESI: 465 (8.5, $[M + H]^+$), 463 (1), 413 (3), 262 (4), 242 (100) | ESI: for $[M + H]^+$ $C_{18}H_{14}N_2O_6P^{80}Se$ calcd. 464.9755, found: 464.9769 | Film: 1615, 1590, 1523, 1488, 1346, 1200, 1160, 1112, 903, 859, 744, 685, 638 |
| **6c** | ESI: 537 (1, contaminant), 535 (3, contaminant), 533 (4, contaminant), 531 (1, contaminant), 435 (50, $[M + H]^+$), 433 (10), 327 (75), 325 (15), 311 (100), 309 (21), 247 (30) | ESI: for $[M + H]^+$ $C_{20}H_{20}O_4P^{80}Se$ calcd. 435.0264, found: 435.0235 | Film: 1501, 1250, 1178, 1116, 1032, 904, 831, 800, 725, 691, 570, 520 |
| **6d** | EI: 512 (9), 511 (10), 510 (44, M), 508 (23), 507 (8). 506 (8), 491 (5), 489 (3), 349 (34), 347 (17), 285 (100), 271 (28), 269 (26), 206 (6), 188 (9), 187 (7), 145 (8), 107 (8), 77 (8) | EI: for M $C_{20}H_{13}F_6O_2P^{80}Se$ calcd.: 509.97226, found: 509.97147 | KBr: 1611, 1510, 1440, 1420, 1325, 1215, 1200, 1170, 1117, 1066, 1020, 910, 845, 722, 626, 590 |

*(Continued)*

**TABLE 3** (Continued)

| *Compound* | *MS (m/z, int%)* | *HR MS* | *IR (ν, cm$^{-1}$)[b]* |
|---|---|---|---|
| **6e** | ESI: 425 (100, $[M + Na]^+$), 423 (25) | ESI: for $[M + Na]^+$ $C_{20}H_{19}O_2P^{80}SeNa$ calcd.: 425.0186, found: 425.0187 | Film 1602, 1503, 1438, 1186, 1160, 1114, 1018, 906, 821, 750, 725, 691, 566 |
| **6f** | ESI: 537 (30, M + Na + 4), 535 (M + Na + 2, 100, M + 2), 533 (98, $[M + Na]^+$), 531 (20, M + Na – 2) | ESI: for $[M + Na]^+$ $C_{18}H_{11}Cl_4O_2P^{80}SeNa$ calcd: 532.8314, found: 532.8301 | KBr: 1472, 1252, 1217, 1120, 1099, 1056, 901, 822, 798, 735, 689, 650, 565, 540 |
| **7** | EI: 530 (3, M), 528 (2), 374 (19), 319 (3), 310 (47), 309 (55), 235 (71), 223 (51), 222 (10), 217 (100), 203 (15), 201 (8), 170 (30),154 (97), 141 (14), 140 (19), 124 (12), 109 (9), 94 (79), 78 (50), 77 (79), 74 (24), 68 (4), 65 (11), 58 (14), 56 (14), 55 (18), 41 (19) | EI: for M $C_{24}H_{39}N_2O_4P^{80}Se$ calcd: 530.18127, found: 530.18330 | KBr: 965, 566, 547 |
| **8c** | EI: 348 (46), 346 (100, M), 344 (49), 343 (17), 342 (18), 311 (3), 265 (7), 231 (10), 225 (9), 223 (19), 221 (10), 189 (22), 187 (74), 185 (37), 184 (15), 183 (14), 161 (18), 159 (59), 145 (5), 143 (16), 123 (96), 109 (16), 107 (24), 95 (30), 77 (28); ESI [a)]: 365 (75, $[M + Na]^+$), 363 (20), 347 (20), 343 (100, $[M + H]^+$), 341 (20), 311 (15) | ESI[a]: for $[M + Na]^+$ $C_{14}H_{15}O_3P^{80}SeNa$: calcd.: 364.9822, found: 364.9731 | KBr: 1500, 1440, 1252, 1178, 1104, 1026, 903, 828, 760, 720, 693, 577 |

[a]Because of the performing the MS ESI spectra of **1b** and **8c** in methanol solution, in fact the spectrum of $PhP(Se)(OCH_3)_2$ (M = 250) is recorded, instead the spectrum of $PhP(Se)Cl_2$ (**1b**, M = 258), and the spectrum of $PhP(Se)(OC_6H_4OCH_3)(OCH_3)$ (M = 342) is recorded, instead the spectrum of $PhP(Se)(CH_3OC_6H_4O)Cl$ (**8c**, M = 346).
[b]Frequency of the P=Se vibrations: 580–590 [21], 504–535, and 565–577 cm$^{-1}$ [22].

The chemical shift of P atom (relative to $H_3PO_4$) and especially of a selenium atom (relative to $(CH_3)_2Se$) in **1b, 6, 8** depends on a number of chlorine and oxygen atoms connected to the phosphorus atom: **1b**: $\delta_P$ = 59.41 ppm, $\delta_{Se}$ = 148.6 ppm, **8**: $\delta_P$ = 84–86 ppm, $\delta_{Se}$ = −36 to −40 ppm, **6**: $\delta_P$ = 92–95 ppm, $\delta_{Se}$ = −242 to −245 ppm.

The observed coupling constants of P=Se bond (910–940 Hz) are in good agreement with the literature data: 852–1064 Hz [23] reported for *O*-acyl

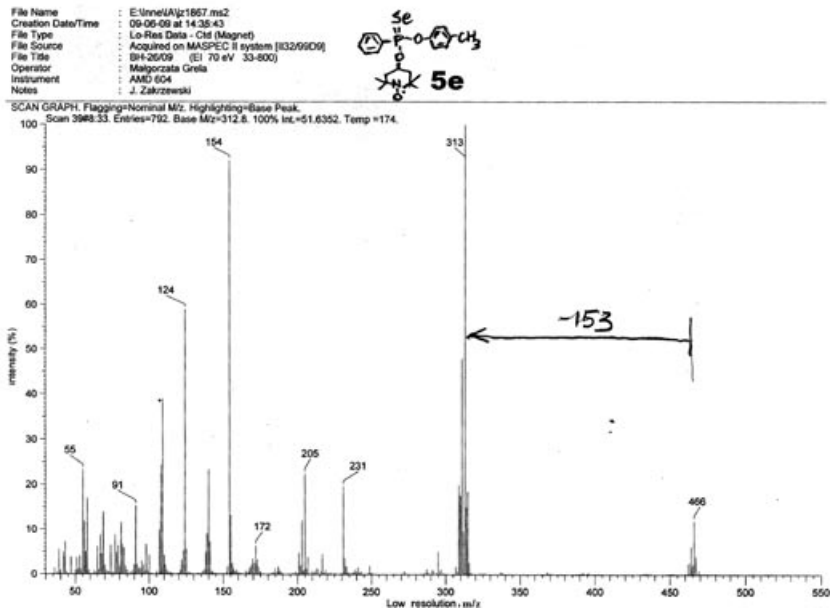



**FIGURE 1** EI MS of **5e**.

**TABLE 4** $^{1}H$, $^{13}C$, $^{31}P$, and $^{77}Se$ NMR Data for the Investigated Compounds

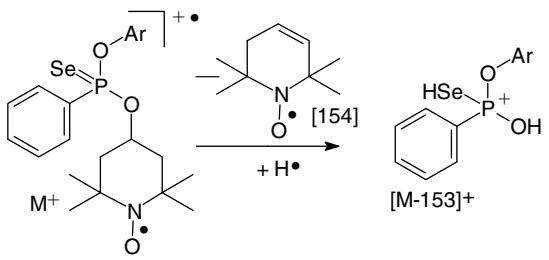
| *Compound* | *$^{1}H$ NMR (500 MHz, $CDCl_3$)* | *$^{13}C$ NMR (125 MHz, $CDCl_3$)* | *$^{31}P$ NMR[a] (202.5 MHz)* | *$^{77}Se$ NMR[a] (95.4 MHz)* |
|---|---|---|---|---|
| **1b** | 7.50–7.61 (m, 2H, $C_6H_5$), 7.62–7.67 (m, 1H), 8.12–8.21 (dm, 2H, $J_{PH}$ = 19.2 Hz) | 128.69 (d, $J_{CP}$ = 17.1 Hz), 130.34 (d, $J_{CP}$ = 14.7 Hz), 133.83 (d, $J_{CP}$ = 3.9 Hz), 138.88 (d, $J_{CP}$ = 100.1 Hz) | 59.41 (s, $J_{PSe}$ = 935 Hz) | 148.6 (dd, $J_{PSe}$ = 935 Hz, $J$ = 4.4 Hz) |
| **6a** | 7.15–7.27 (m, 5H), 7.29–7.46 (m, 5H), 7.54–7.62 (m, 2H, P-$C_6H_5$), 7.62–7.68 (m, 1H, P-$C_6H_5$), 8.17–8.26 (m, 2H, P-$C_6H_5$) | 121.77 (d, $J_{CP}$ = 4.7 Hz, 4 × $CH_{ar}$ /*o*-O/), 125.14 (d, $J_{CP}$ = 1.9 Hz, 2 × $CH_{ar}$ /*p*-O/), 128.34 (d, $J_{CP}$ = 15.4 Hz), 129.23 (d, $J_{CP}$ = 1.5 Hz, 4 × $CH_{ar}$ /*m*-O/), 131.38 (d, $J_{CP}$ = 12.8 Hz, 2 × $CH_{ar}$ /*m*-P/), 132.87 (d, $J_{CP}$ = 3.1 Hz, $CH_{ar}$ /*p*-P/), 134.20 (d, $J_{CP}$ = 134.9 Hz, C-P), 150.69 (d, $J_{CP}$ = 8.7 Hz, 2 × COP) | 92.60 (s, $J_{PSe}$ = 914 Hz) | –244.17 (d, $J_{PSe}$ = 914 Hz) |
| **8a**[b] | – | 121.66 (d, $J_{CP}$ = 5.4 Hz), 126.08 (d, $J_{CP}$ = 2.5 Hz), 128.47 (d, $J_{CP}$ = 17.6 Hz), 129.53 (d, $J_{CP}$ = 2 Hz), 130.58 (d, $J_{CP}$ = 13.6 Hz), 133.33 (d, $J_{CP}$ = 3.5 Hz), 136.29 (d, $J_{CP}$ = 123.0 Hz), 150.05 (d, $J_{CP}$ = 11.2 Hz) | 83.99 (s, $J_{PSe}$ = 932 Hz) | –37.07 (d, $J_{PSe}$ = 932 Hz) |
| **6b** | 7.26–7.30 (m, 3H), 7.36 (s, 2H), 7.58–7.65 (m, 2H, P-$C_6H_5$), 7.66–7.74 (m, 1H, P-$C_6H_5$), 8.12–8.20 (m, 2H, P-$C_6H_5$), 8.21–8.25 (m, 3H) | 122.49 (d, $J_{CP}$ = 4.9 Hz, 4 × $CH_{ar}$ /*m*-$NO_2$/), 125.40 (d, $J_{CP}$ = 1.1 Hz, 4 × $CH_{ar}$ /*o*-$NO_2$/), 128.89 (d, $J_{CP}$ = 15.7 Hz, 2 × $CH_{ar}$ /*o*-P/), 131.59 (d, $J_{CP}$ = 13.3 Hz, 2 × $CH_{ar}$/*m*-P/), 132.54 (d, $J_{CP}$ = 133.6 Hz/C-P/), 134.03 (d, $J_{CP}$ = 3.3 Hz, $CH_{ar}$/*p*-P/), 145.23 (d, $J_{CP}$ = 1.9 Hz, 2 × C-$NO_2$), 154.99 (d, $J_{CP}$ = 7.9 Hz, 2 × COP) | 94.14 (s, $J_{PSe}$ = 933 Hz) | –237.18 (d, $J_{PSe}$ = 933 Hz) |
| **8b**[b] | – | 122.60 (d, $J_{CP}$ = 5.8 Hz), 128.73 (d, $J_{CP}$ = 16.7 Hz), 130.72 (d, $J_{CP}$ = 14.0 Hz), 133.89 (d, $J_{CP}$ = 3.65 Hz), 154.57 (d, $J_{CP}$ = 11.3 Hz) | 84.13 (s, $J_{PSe}$ = 940 Hz) | –36.07 (d, $J_{PSe}$ = 942 Hz) |
| **6c** | 3.77 (s, 6H, 2 × $OCH_3$), 6.81–6.85 (m, 4H, $OC_6H_4O$), 7.01–7.06 (m, 4H, $OC_6H_4O$), 7.52–7.57 (m, 2H, $C_6H_5$-P), 7.59–7.64 (m, 1H, $C_6H_5$-P), 8.11–8.17 (dm, 2H, $J_{PH}$ = 14.9 Hz, $C_6H_5$-P). | 55.46 (s, 2 × $OCH_3$), 114.35 (d, $J_{CP}$ = 1.6 Hz, 4 × $CH_{ar}$ /*o*-$OCH_3$/), 122.65 (d,$J_{CP}$ = 4.4 Hz, 4 × $CH_{ar}$ /*m*-$OCH_3$/), 128.33 (d, $J_{CP}$ = 15.1 Hz, 2 × $CH_{ar}$ /*o*-P/), 131.48 (d, $J_{CP}$ = 12.6 Hz, 2 × $CH_{ar}$ /*m*-P/), 132.84 (d, $J_{CP}$ = 3.1 Hz, $CH_{ar}$ /*p*-P/), 134.28 (d, $J_{CP}$ = 134.2 Hz, /C-P/), 144.24 (d, $J_{CP}$ = 8.8 Hz, 2 × COP), 156.95 (d, $J_{CP}$ = 2.0 Hz, 2 × $COCH_3$) | 94.47 (s, $J_{PSe}$ = 908 Hz) | –249.65 (d, $J_{PSe}$ = 908 Hz) |

*(Continued)*

**TABLE 4** (Continued)

| *Compound* | *$^1$H NMR (500 MHz, $CDCl_3$)* | *$^{13}$C NMR (125 MHz, $CDCl_3$)* | *$^{31}$P NMR[a] (202.5 MHz)* | *$^{77}$Se NMR[a] (95.4 MHz)* |
|---|---|---|---|---|
| **8c**[c] | 3.78 (s, 3H, $OCH_3$), 6.87–6.91 (m, 2H, $OC_6H_4O$), 7.21–7.25 (m, 2H, $OC_6H_4O$), 7.52–7.57 (m, 2H, $C_6H_5$-P), 7.59–7.64 (m, 1H, $C_6H_5$-P), 8.12–8.19 (dm, 2H, $J_{PH} = 16.7$ Hz, $C_6H_5$-P) | 55.53 (s, $OCH_3$), 114.52 (d, $J_{CP} = 2.1$ Hz, 2 × $CH_{ar}$ /*o*-$OCH_3$/), 122.60 (d, $J_{CP} = 5.2$ Hz, 2 × $CH_{ar}$ /*m*-$OCH_3$/), 128.49 (d, $J_{CP} = 16.4$ Hz, 2 × $CH_{ar}$ /*o*-P/), 130.68 (d, $J_{CP} = 13.6$ Hz, 2 × $CH_{ar}$ /*m*-P/), 133.35 (d, $J_{CP} = 3.5$ Hz, $CH_{ar}$/*p*-P/), 136.31 (d, $J_{CP} = 122.6$ Hz,/C-P/), 143.51 (d, $J_{CP} =$ 11.4 Hz, 2 × COP), 157.55 (d, $J_{CP} = 2.5$ Hz, 2 × $COCH_3$) | 85.51 (s, $J_{PSe} =$ 930 Hz) | –39.98 (d, $J_{PSe} =$ 930 Hz) |
| **6d** | 7.20–7.24 (m, 4 H), 7.54–7.62 (m, 6 H), 7.68 (pseudo tq, 1H, $J = 7.5$ Hz, $J = 1.5$ Hz), 8.11–8.18 (dm, 2H, $J_{PH} =$ 15.5 Hz) | 122.26 (d, $J_{CP} = 4.8$ Hz, $CH_{ar}$ /*m*-$CF_3$/), 123.82 (q, $J_{CF} =$ 271.8 Hz, $CF_3$), 126.99 (qd, $J_{CF} = 3.9$ Hz, $J_{CP} = 1.5$ Hz, $CH_{ar}$ /*o*-$CF_3$/), 127.96 (qd, $J_{CF} = 32.7$ Hz, $J_{CP} = 1.9$ Hz, Car /C–$CF_3$/), 128.76 (d, $J_{CP} =$ 15.7 Hz, $CH_{ar}$/*o*-P/), 131.63 (d, $J_{CP} = 13.1$ Hz, $CH_{ar}$/*m*-P/), 133.32 (d, $J_{CP} = 134.2$ Hz, $C_{ar}$/C–P/), 133.66 (d, $J_{CP} =$ 3.4 Hz, $CH_{ar}$/*p*-P/), 153.02 (dq, $J_{CP} = 6.3$ Hz, $J_{CF} = 1.4$ Hz, $C_{ar}$/C–O/) | 93.64 (s, $J_{PSe} =$ 926 Hz) | –242.51 (d, $J_{PSe} = 926$ Hz) |
| **6e** | 2.29 (s, 6H, 2 × $CH_3$), 6.95–7.00 (m, 4H, $OC_6H_4CH_3$), 7.05–7.10 (m, 4H, $OC_6H_4CH_3$), 7.49–7.54 (m, 2H, $C_6H_5$-P), 7.55–7.60 (m, 1H, $C_6H_5$-P), 8.08–8.16 (dm, 2H, $J_{PH} = 15.5$ Hz, $C_6H_5$-P). | 20.79 (s, 2 × $CH_3$), 121.55 (d, $J_{CP} = 4.9$ Hz, 4 × $CH_{ar}$/*m*-$CH_3$/), 128.36 (d, $J_{CP} = 15.1$ Hz, 2 × $CH_{ar}$/*o*-P/), 129.92 (d, $J_{CP} = 1.9$ Hz, 4 × $CH_{ar}$/*o*-$CH_3$/), 131.48 (d, $J_{CP} = 12.7$ Hz, 2 × $CH_{ar}$/*m*-P/), 132.84 (d, $J_{CP} = 3.4$ Hz, $CH_{ar}$/*p*-P/) 134.43 (d, $J_{CP} =$ 134.43 Hz,/C-P/), 134.99 (d, $J_{CP} = 2.4$ Hz, /C-$CH_3$/), 148.56 (d, $J_{CP} = 8.7$ Hz, 2 × COP) | 92.67 (s, $J_{PSe} =$ 910 Hz) | –247.26 (d, $J_{PSe} = 910$ Hz) |
| **6f** | 7.17 (dd, 2H, $J = 8.8$ Hz, $J = 2.5$ Hz, $POC_6H_3Cl_2$), 7.22 (dd, 2H, $J = 8.8$ Hz, $J_{PH} = 2.0$ Hz, $POC_6H_3Cl_2$), 7.42 (d, 2H, $J =$ 2.5 Hz, $POC_6H_3Cl_2$), 7.54–7.60 (m, 2H, $C_6H_5$-P), 7.63–7.68 (m, 1H, $C_6H_5$-P), 8.19–8.26 (dm, 2H, $J_{PH} =$ 15.5 Hz, $C_6H_5$-P) | 124.04 (d, $J_{CP} = 3.9$ Hz, 2 × $CH_{ar}$ /$C_6H_3Cl_2$/), 127.64 (d, $J_{CP} = 1.9$ Hz, 2 × $CH_{ar}$ /$C_6H_3Cl_2$/), 127.88 (d, $J_{CP} =$ 5.3 Hz, 2 × Car /$C_6H_3Cl_2$/), 128.55 (d, $J_{CP} = 15.6$ Hz, 2 × $CH_{ar}$ /*o*-P/), 130.38 (d, $J_{CP} =$ 2.0 Hz, 2 × $CH_{ar}$ /$C_6H_3Cl_2$/), 131.24 (d, $J_{CP} = 2.4$ Hz, 2 × Car /$C_6H_3Cl_2$/), 131.74 (d, $J_{CP} = 13.2$ Hz, 2 × $CH_{ar}$ /*m*-P/), 133.37 (d, $J_{CP} = 136.7$ Hz, /C-P/), 133.57 (d, $J_{CP} = 3.4$ Hz, $CH_{ar}$ /*p*-P/), 145.71 (d, $J_{CP} = 8.3$ Hz, 2 × COP) | 94.76 (s, $J_{PSe} =$ 931 Hz) | –244.19 (d, $J_{PSe} = 931$ Hz) |

[a]P═Se coupling constants are calculated from the $^{77}$Se NMR spectrum, as well as compared with the satellite bands observed in $^{31}$P NMR spectrum.
[b]ot isolated; observed in $^{13}$C NMR spectrum of diaryl esters.
[c]solated.




**SCHEME 4** M-153 fragment observed in mass spectra of **5a–f**.

selenophosphates ($R^1R^2P(=Se)OCOR^3$). For comparison, the coupling constant of the P=Se bond for $(CH_3O)Ph_2P=Se$ and $(CH_3O)_2PhP=Se$ are reported as 788 and 881 Hz, respectively [24].

The plant protection activity of the synthesized phenylselenophosphonic aryl nitroxyl esters **5a–f** and phenylselenophosphonic diaryl esters **6a–f** was evaluated. All the synthesized compounds (**5a–f**, **6a–f**) were inactive as herbicides and insecticides, but some of them showed antifungal activity. The inhibition effect of selenium derivatives on phytopathogenic fungi was studied by a method previously described [25] using five species: *Botrytis cinerea, Fusarium culmorum, Phytophthora cactorum, Rhizoctonia solani*, and *Blumeria graminis*. Three fungicides, chlorothalonil (2,4,5,6-tetrachloroisophthalonitrile, CAS: 1897-45-6)), carboxin (5,6-dihydro-2-methyl-1,4-oxathiine-3-carboxanilide, CAS: 5234-68-4), and metconazole (5-[(4-chlorophenyl)methyl]-2,2-dimethyl-1-(1*H*-1,2,4-triazol-1-ylmethyl)cyclopentanol, CAS: 125116-23-6), were used as the reference compounds. The results of the evaluation are shown in Table 5.

The antifungal activity of some obtained derivatives was observed. The investigated compounds generally showed a weak to good broad-spectrum activity against several plant diseases. It was found that the monoester with a 4-$CH_3$ group (**5e**) showed the highest level of protection against *R. solani* and against *B. cinerea,* and a moderate inhibition effect against *P. cactorum*, at the concentration of 200 mg/L. Probably, introduction of the methyl groups in the compound increases the lipophilicity and improves absorption into a cell membrane. The activating character of a methyl group is known for the mode of action of some herbicides and fungicides. Lipophilic herbicides more readily diffuse across the membrane than hydrophilic ones do [26]. Two selenium derivatives, monoester and diester bearing a nitro group (**5b, 6b**), exhibited 100% reduction of *R. solani* mycelium growth, and a remarkable growth inhibition of two other species: *P. cactorum* (**5b**) or *B. cinerea* (**6b**).

Moreover, a diester **6d** with a trifluoromethyl group shows a moderate activity against *R. solani*. The compounds, **6a** and **6c**, reduced growth of powdery mildew on wheat (*B. graminis*), whereas they were devoid of any antifungal activity against the rest of the pathogens. The compound **6e** was inactive in a preliminary test toward all the tested fungal strains. Three compounds **5b, 6b**, and **5e** have better antifungal activity against *R. solani* than the commercial fungicide chlorothalonil. The most active compound **5e** displayed better activity against *B. cinerea* and was comparable against *P. cactorum* with the chlorothalonil, but all of the compounds were inferior to the commercial fungicide carboxine.

## *CONCLUSIONS*

In conclusion, we proposed a novel and efficient method to synthesize *O*-aryl phenylselenophosphonates bearing a nitroxyl moiety **5a–f** using phenyldichlorophosphine selenide (**1b**) as a key intermediate. The application of **1b** results in much better yields than the method where phenyldichlorophosphine (**1a**) and black selenium are used. Some selenophenylphosphonates bearing a nitroxyl moiety **5a–f** and diaryl selenophenylphosphonates **6a–f** showed a weak to good antifungal activity in vitro against *B. cinerea, F. culmorum, P. cactorum,* and *R. solani* and in vivo against *B. graminis*. Monoester with the 4-$CH_3$ group and mono- and diester with the 4-$NO_2$ group were particularly active in inhibition of *R. solani* mycelium growth.

## *EXPERIMENTAL*

### *General*

2,2,6,6-Tetramethyl-4-piperidinol-1-oxyl (**2**) was synthesized by oxidation of 2,2,6,6-tetramethyl-4-piperidinol with 30% hydrogen peroxide (76.5%, mp 71–73°C) according to methods described in [27–29]. Phenyldichlorophosphine and phenols **3a–f** was purchased from Aldrich and used without further purification. All experiments were performed in a three-necked flask of 25 mL capacity protected from humidity (a tube with calcium chloride) and air (dry argon), equipped with a magnetic bar, a thermometer, a dropping funnel, a reflux condenser, and an ice-salt bath (with exception of **1b** synthesis where a silicon oil bath was used). TLC monitoring and column chromatography were done on Merck silica gel Alurolle 5562, Alufolien 5554, and Merck

**TABLE 5** Antifungal Activity of **5a–f, 6a–f**, and **7** (**R•** = Nitroxyl Moiety). Reduction of the Colonies Growth (%)

| # | Compound | *B. cinerea*, 200 mg/L in vitro | *F. culmorum*, 200 mg/L in vitro | *P. cactorum*, 200 mg/L in vitro | *R. solani*, 200 mg/L in vitro | *B. graminis*, 1000 mg/L in vivo |
|---|---|---|---|---|---|---|
| **5a** | (Ph)($OC_6H_5$)(O**R•**) PSe | 0 | 0 | 14 | 9 | 34 |
| **6a** | (Ph)($OC_6H_5$)$_2$PSe | 0 | 0 | 0 | 2 | 84 |
| **5b** | (Ph)(O**R•**) ($OC_6H_4NO_2$)PSe | 37 | 17 | 54 | 91 | 0 |
| **6b** | (Ph)($OC_6H_4NO_2$)$_2$PSe | 66 | 14 | 10 | 100 | 32 |
| **5c** | (Ph)(O**R•**) ($OC_6H_4OCH_3$)PSe | 4 | 0 | 13 | 0 | 0 |
| **6c** | (Ph)($OC_6H_4OCH_3$)$_2$PSe | 0 | 0 | 5 | 0 | 51 |
| **5d** | (Ph)(O**R•**) ($OC_6H_4CF_3$)PSe | 0 | 0 | 24 | 28 | 0 |
| **6d** | (Ph)($OC_6H_4CF_3$)$_2$PSe | 0 | 0 | 0 | 62 | 26 |
| **5e** | (Ph)(O**R•**) ($OC_6H_4CH_3$)PSe | 95 | 41 | 61 | 100 | 0 |
| **6e** | (Ph)($OC_6H_4CH_3$)$_2$PSe | 0 | 0 | 0 | 0 | 0 |
| **5f** | (Ph)(O**R•**) ($OC_6H_3Cl_2$)PSe | 21 | 0 | 0 | 21 | 0 |
| **6f** | (Ph)($OC_6H_3Cl_2$)$_2$PSe | 25 | 0 | 0 | 25 | 0 |
| **7** | (Ph)(O**R•**)$_2$ PSe | 25 | 10 | 4 | 9 | 21 |
| | Chlorothalonil | 76 | 38 | 61 | 85 | – |
| | Carboxin | 100 | 80 | – | 100 | – |
| | Metconazole | – | – | – | – | 100 |

1.09385.1000 (0.040–0.063 mm, 230–400 mesh), respectively. The following abbreviations for mobile phases were used throughout the text: HxA4, HxA9 = hexane: ethyl acetate 4:1, 9:1, respectively, BA4, BA9 = benzene: ethyl acetate 4:1, 9:1, respectively. The progress of the reactions was monitored by means of TLC (silica gel plates (Merck 5562, 5554), mobile phase: HxA4, HxA9). Visualization of TLC plates: UV 254, and/or iodine vapors, and/or spraying with 1% ethanolic $PdCl_2$. MS (EI, 70 eV, *m/z*, int. (%)) data were recorded using an AMD 604 and Agilent Technologies 5975 B mass spectrometers. HR MS (EI) data were recorded using an AMD 604 mass spectrometer. MS and HR MS (ESI, positive ions, $CH_3OH$ as a solvent) were recorded using Micromass LCT apparatus. IR ($\nu$, $cm^{-1}$) data were recorded using a FT/IR Jasco 420 spectrophotometer. NMR data were collected using Varian UNITYplus 200, Varian UNITYplus 500 ($^1H$, $^{13}C$, $^{31}P$), and Bruker DRX 500 Advance [$^1H$, $^{13}C$, $^{31}P$, $^{77}Se$ (referenced to $(CH_3)_2Se$)].

The methods for assessing antifungal activity involving both in vitro and in vivo tests were identical to those previously published [25].

### *Phenyldichlorophosphine Selenide (***1b***)*

Phenyldichlorophosphine (**1a**, 8.95 g, 0.05 mol, 6.8 mL) and black selenium (4.75 g, 0.06 mol) were stirred for 1.5 h at 175–180°C. After the reaction had been terminated, the unreacted selenium was filtered off under reduced pressure through a pad of white cellulose wool and a cotton wool plug. Alternatively, filtration through Cellite bed followed by washing with diethyl ether may be used. The filtrate was subjected to distillation followed by redistillation under reduced pressure (diffusion pump) to give phenyldichlorophosphine selenide (**1b**, 7.697 g, 59.7%, bp 68–74°C/0.01 mmHg (60°C/0.01 mmHg [19], 79°C/0.04 mmHg [20]).

### *Phenylselenophosphonic 2,2,6,6-Tetramethyl-1-oxyl-4-oxypiperidyl Chloride (***4***)*

Phenyldichlorophosphine selenide (**1b**, 2.5 mmol, 0.645 g, 0.4 mL) in dry ether (10 mL) was cooled down to 0–5°C. The solution of 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl (**2**, 2.5 mmol, 0.430 g) and pyridine (2.5 mmol, 0.189 g, 0.2 mL) in ether (5 mL) was added dropwise. The reaction mixture was stirred for 2 h at room temperature. After the reaction had been terminated, the precipitate of pyridinium hydrochloride was filtered off. The filtrate was concentrated to dryness. The residue (1.078 g) was subjected to column chromatography (mobile phase: benzene) to give **4** (0.349 g, 35.4%, mp 42–52°C).

### *Phenylselenophosphonates* **5a–f** *from Phenyldichlorophosphine (***1a***) (Method A)*

Phenyldichlorophosphine (**1a**, 2.5 mmol, 0.339 g, 0.34 mL) in dry ether (10 mL) was cooled down to 0–5°C. A solution of the appropriate phenol (**3a–f**, 2.5 mmol) and pyridine (2.5 mmol, 0.189 g, 0.2 mL) in ether (3 mL) was added dropwise into

the reaction mixture. After 5 min, the solution of 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl (**2**, 0.430 g, 2.5 mmol) and pyridine (2.5 mmol, 0.189 g, 0.2 mL) in ether (5 mL) was added dropwise. The mixture was stirred for 15 min, and black selenium (0.5 g, 6.3 mmol) was added. After approximately 2 h, the second portion of selenium (0.5 g, 6.3 mmol) was added. The reaction mixture was stirred for 20 h at room temperature. After the reaction had been terminated, the suspension was filtered through silica bed of 1-cm height. The filtrate was concentrated to dryness. The residue was subjected to column chromatography (mobile phase: HxA4, HxA9, BA4, BA9) to give **5a–f**, **6a–f**, and **7**.

### *Selenophenylphosphonates* **5a–f** *from Phenyldichlorophosphine Selenide (***1b***) (Method B)*

Phenyldichlorophosphine selenide (**1b**, 2.5 mmol, 0.645 g, 0.4 mL) in dry ether (10 mL) was cooled down to 0–5°C. Appropriate solution of phenol (**3a-f**, 2.5 mmol) and pyridine (2.5 mmol, 0.189 g, 0.2 mL) in ether (3 mL) was added dropwise into the reaction mixture. After 5 min, the solution of 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl (**2**, 0.430 g, 2.5 mmol) and pyridine (2.5 mmol, 0.189 g, 0.2 mL) in ether (5 mL) was added dropwise. The reaction mixture was stirred for 2 h at room temperature. After the reaction had been terminated, the pyridinium hydrochloride was filtered off. The filtrate was concentrated to dryness. The residue was subjected to column chromatography (mobile phase: HxA4, HxA9, BA4, BA9) to give **5a–f**, **6a–f** and **7**.

### *Diaryl selenophenylphosphonates* **6a–f** *from Phenyldichlorophosphine Selenide (***1b***) (Method B)*

Phenyldichlorophosphine selenide (**1b**, 2.5 mmol, 0.645 g, 0.4 mL) in dry ether (10 mL) was cooled down to 0–5°C. Appropriate solution of phenol (**3a–f**, 5 mmol) and pyridine (5 mmol, 0.378 g, 0.4 mL) in ether (5 mL) was added dropwise into the reaction mixture. The reaction mixture was stirred for 2 h at room temperature. After the reaction had been terminated, the pyridinium hydrochloride was filtered off. The filtrate was concentrated to dryness. The residue was subjected to column chromatography (mobile phase: HxA4, HxA9, BA4, BA9) to give **6a–f**.

### *Phenylselenophosphonic (4-methoxyphenoxy) chloride (***8c***)*

Phenyldichlorophosphine selenide (**1b**, 1.25 mmol, 0.322 g, 0.2 mL) in dry ether (10 mL) was cooled down to 0–5°C. The solution of 4-methoxyphenol (0.310 g, 2.5 mmol) and pyridine (2.5 mmol, 0.189 g, 0.2 mL) in ether (5 mL) was added dropwise. The reaction mixture was stirred for 5.5 h at room temperature. After the reaction had been terminated, the precipitate of pyridinium hydrochloride was filtered off. The filtrate was concentrated to dryness. The residue (0.589 g) was subjected to column chromatography (mobile phase: HxA9) to give **8c** (0.2 g, 46.3%, mp 45–48°C) and **6c** (0.295 g, 54.5%).

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