Small Organophosphorus–Selenium Heterocycles from the Selenation of Conjugated Ketones and Enals

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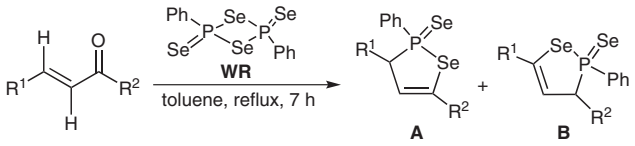
Abstract: Reaction of 2,4-bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide [Woollins' reagent, **WR**] with equimolar amount of α,β-unsaturated ketones [$R^1C(O)C{=}CR^2$ (R^1 = aryl or alkyl; R^2 = aryl)] leads to a series of novel five-membered $C_3P(Se)Se$ heterocycles **1**–**8** in 48–95% isolated yields. Furthermore, **WR** reacts with one equivalent of aromatic conjugated enals [RC=CC=O, R = Ph and 2-$MeOC_6H_4$] to give five-membered $C_3P(Se)Se$ heterocycles **9** and **10** via the cleavage/cyclic extension of **WR** molecular ring. All new compounds have been characterised spectroscopically (^{31}P NMR, ^{77}Se NMR, ^1H NMR, ^{13}C NMR, IR and mass spectroscopy) and one representative X-ray structure is reported.

Key words: selenium, phosphorus, heterocycles, Woollins' reagent, X-Ray structure

The synthesis of selenium-containing heterocyclic compounds has gained considerable attention in recent years, because of their interesting reactivities and potential pharmaceutical properties,[1,2] new materials[3] as well as reagents and catalysts.[4] However, synthesis of selenium-containing organic heterocycles is not always easy due to the inconvenience of typical selenium reagents such as H_2Se, NaHSe, $(Me_3Si)_2Se$, potassium selenocyanate and tetraethylammonium tetraselenotungstate $[Et_4N]_2WSe_4$, each exhibiting its own problems including toxicity, solubility, difficulty in handling and poor reactivity. 2,4-Bis(phenyl)-1,3-diselenadiphosphetane-2,4-diselenide $[PhP(Se)(\mu\text{-}Se)]_2$, known as Woollins' reagent, **WR**, has become an efficient selenation reagent in synthetic chemistry in recent years[5] due to its less unpleasant chemical properties and ready preparation in air.[6] **WR** has been applied as a selenation agent for the synthesis of a wide selenium-containing compounds ranging from simple oxygen–selenium exchange to the formation of complex phosphorus–selenium heterocycles[5–14]as well as the surprising phosphorus–selenium-free products.[15,16]

In continuation of our studies designed to explore the reactivity of **WR** towards a variety of organic substituents as building blocks for heterocyclic compounds, herein, we report the synthesis and characterisation of a series of novel organophosphorus–selenium heterocycles from reaction of **WR** with α,β-unsaturated ketones and enals.

The synthesis of five-membered heterocycles **1**–**8** was performed via the reaction of **WR** with one equivalent of α,β-unsaturated ketones according to Scheme 1. No obvious differences of yield were found when the reaction of **WR** with two or more equivalents of α,β-unsaturated ketones was carried out. That means the reaction straightforwardly generates unique five-membered ring systems. Cleavage of the four-membered P_2Se_2 ring in **WR** affords **1**–**8** in good to excellent yields as pastes or solids (Table 1). All compounds are soluble in chlorinated solvents and stable in air for months without any signals of degradation.



Scheme 1 Synthesis of five-membered heterocycles **1**–**8** from the selenation of α,β-unsaturated ketones

Table 1 Yields of Se-Alkyl-*O*-alkylphenylphosphono Diselenoates **1**–**8**

Product	R^1	R^2	Yield (%)
1	Ph	Ph	92
2	Ph	4-$MeOC_6H_4$	95
3	Me	Ph	81
4	4-MeC_6H_4	4-FC_6H_4	84
5	PhCH=CH	Ph	83
6	thiophen-2-yl	4-$O_2NC_6H_4$	67
7	Me_2N	3-BrC_6H_4	50
8	thiophen-2-yl	thiophen-2-yl	48

The characterisation of **1**–**8** is based on their ^1H NMR, ^{13}C NMR, ^{31}P NMR and ^{77}Se NMR, IR spectroscopy, mass spectrometry and elemental microanalysis. All of compounds showed the anticipated molecular ion peaks $[M + Na]^+$, $[M + H]^+$ or $[M]^+$, and satisfactory accurate mass measurements or satisfactory elemental analysis. The phosphorus atom and the tetrahedral carbon atom in compounds **1**–**8** are potentially stereogenic centres. Thus, compounds **1**–**8** are stereotopic with (*R*,*R*), (*S*,*S*), (*S*,*R*) and (*R*,*S*) stereoisomers possible. In the ^{31}P NMR spectra of **1**, **2**, **4**, **5** and **7** two phosphorus signals with different intensity ratio (see experiment section) were observed at

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δ_P = 56.1–73.0 ppm, flanked by two sets of satellites for the endocyclic and exocyclic selenium atoms [J(P,Se$_{indo}$) coupling constants being in the range of 333–369 Hz and J(P,Se$_{exo}$) coupling constants in the range of 782–806 Hz] though we are not able to assign them specifically to (*R*,*R*), (*S*,*S*), (*S*,*R*) and (*R*,*S*) stereoisomers. Meanwhile, in the ^{31}P NMR spectra of compound **3**, **6** and **8** four phosphorus signals with different intensity ratios (see experiment section) were found at δ_P = 54.1–75.6 ppm, flanked by two sets of satellites for the endocyclic and exocyclic selenium atoms [J(P,Se$_{indo}$) coupling constants being in the range of 331–390 Hz and J(P,Se$_{exo}$) coupling constants in the range of 765–832 Hz], and suggesting the presence of somewhat less steric effects, compared with compounds **1**, **2**, **4**, **5** and **7**. The ^{77}Se NMR spectra showed two doublet signals in the ranges of δ = 354.9–487.1 ppm and δ = –83.2 to –203.3 ppm for each stereoisomer (Table 2). Attempts to further purify **1**–**8** by recrystallisation proved unsuccessful.

Table 2 ^{31}P NMR and ^{77}Se NMR Data for Compounds **1**–**8**

Product	δ_P (ppm)	$\delta_{Se\text{-}endo}$ (ppm)	$J_{Se–P}$ (Hz)	$\delta_{Se\text{-}exo}$ (ppm)	$J_{Se=P}$ (Hz)
1	72.4	408.9	346	–187.5	806
	71.4	391.5	346	–170.8	786
2	73.0	406.7	336	–188.2	801
	71.6	390.0	345	–174.1	784
3	75.6	443.9	390	–125.9	765
	75.3	421.4	336	–182.8	801
	74.7	405.5	346	–156.7	782
	61.7	449.7	390	–111.7	770
4	72.0	400.7	340	–191.1	803
	70.7	386.5	357	–177.8	789
5	70.3	370.4	338	–188.0	803
	69.9	354.9	350	–170.0	782
6	73.7	414.8	329	–190.8	832
	71.8	405.6	341	–166.7	796
	61.0	473.1	365	–161.5	793
	54.1	487.1	381	–83.2	782
7	57.0	450.0	333	–131.6	787
	56.1	455.2	369	–131.2	785
8	71.1	407.3	336	–203.3	810
	69.1	412.7	341	–176.7	792
	61.0	477.2	377	–166.4	789
	60.5	398.5	393	–142.5	777

The structural features of the new five-membered ring in compound **1A** are analogous to those observed for compound **5A**, whose X-ray structure has been reported previously by our group.[17] The spectroscopic and analytical data are in agreement with the structure of **1A** determined by X-ray crystallography (Figure 1)[18] and its geometry is best described as a distorted 'open envelope' conformation, with one phenyl ring in the equatorial position and two other phenyl rings in axial plane. The atoms Se(1), C(1), C(2) and C(3) which constitute the newly formed five-membered ring in compound **1A**, build up a nearly planar conformation. Meanwhile, the deviation of the P(1) atom from the plane of Se(1)–C(1)–C(2)–C(3) is 0.644 Å. The dihedral angles between the Se(1)–C(1)–C(2)–C(3) and three phenyl rings [C(4)–C(9), C(10)–C(15) and C(16)–C(21)] are 56.9°, 32.8° and 88.6°, respectively. The relative short P(1)–C(4) bond length of 1.830(5) Å, compared to the P(1)–C(3) bond distance [1.862(5) Å], indicates partial double bond character. The distances of P(1)–Se(1) and P(1)–Se(2) of 2.2540(13) Å and 2.0954(13) Å are similar to P–Se and P=Se bond lengths previously observed for other related compounds containing the P(Se)(μ-Se) unit.[19–21]

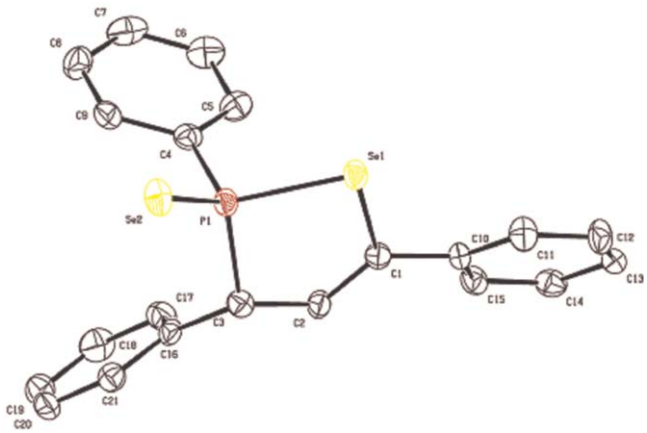
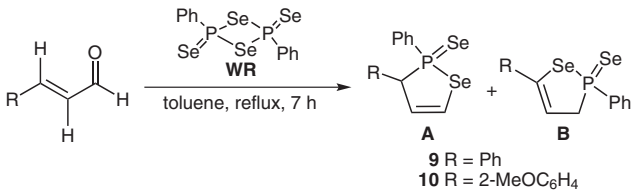


Figure 1 X-ray structure of **1A** (hydrogen atoms omitted for clarity). Selected bond lengths (Å) and angles (°): C(1)–C(2): 1.325(6), C(1)–C(10): 1.486(6), C(1)–Se(1): 1.954(4), Se(1)–P(1): 2.2540(13), Se(2)–P(1): 2.0954(13), P(1)–C(4): 1.830(5), P(1)–C(3): 1.862(5), C(2)–C(3): 1.515(6); C(2)–C(1)–C(10): 127.6(4)°, C(2)–C(1)–Se(1): 116.7(3)°, C(10)–C(1)–Se(1): 115.7(3)°, C(1)–Se(1)–P(1): 88.32(13)°, C(4)–P(1)–C(3): 109.2(3)°, C(4)–P(1)–Se(2): 112.67(15)°, C(3)–P(1)–Se(2): 115.81(15)°, C(4)–P(1)–Se(1): 107.08(15)°, C(3)–P(1)–Se(1): 95.82(14)°, Se(2)–P(1)–Se(1): 115.50(6)°, C(1)–C(2)–C(3): 122.8(4)°.

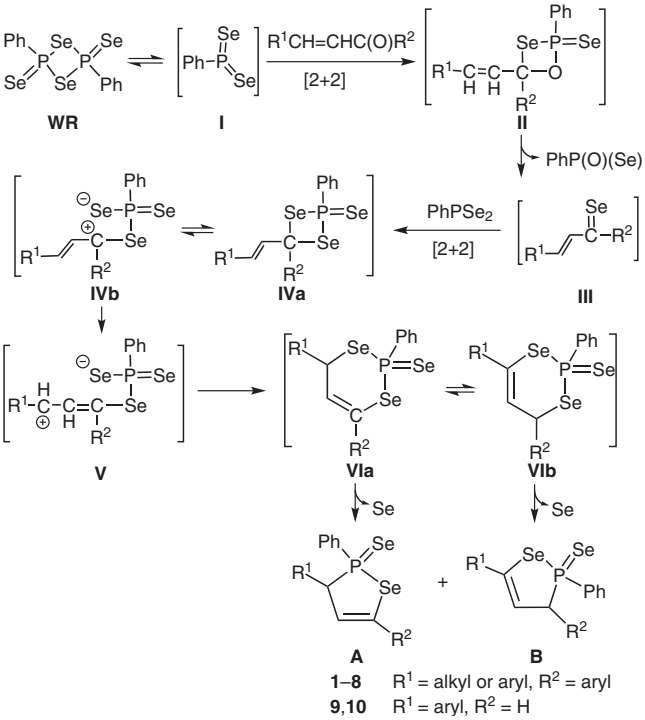
Similarly to Scheme 1, **WR** reacts with one equivalent of aromatic α,β-unsaturated enals in refluxing toluene resulting in the corresponding five-membered phosphorus–selenium heterocycles **9** and **10** in respective 79% and 56% isolated yields (Scheme 2). The compounds were isolated as stable and reddish yellow paste (**9**) or greyish yellow solid (**10**). The molecular ion peaks [M + H]$^+$ and satisfactory accurate mass measurement results, together with NMR data are consistent with the anticipated formulas. Once again, both phosphorus atom and tetrahedral carbon atom in the newly formed five-membered ring in compounds **9** and **10** are potentially chiral centres with (*R*,*R*), (*S*,*S*), (*S*,*R*) and (*R*,*S*) stereoisomers possible. In fact, two stereoisomers were observed in **9**, and four in **10** (see experimental section). The introduction of the bigger bulky group (2-MeOC$_6$H$_4$) or the smaller bulky group (Ph) is reflected in the distribution of stereoisomers in the product.

Mechanistically, we propose a possible pathway for the formation of heterocycles **1**–**10** as shown in Scheme 3.

Similar to its sulfur analogue, Lawesson's reagent[22] **WR** can also undergo four-membered P_2Se_2 ring-opening mechanism with a propensity leading to several types of fragments which were confirmed by mass spectrometry.[23] At elevated temperature $PhPSe_2$ (**I**) is known as the reactive species in solution. The first step in the formation of **1**–**10** is a [2+2]-cycloaddition of a P=Se bond from $PhPSe_2$ (**I**) across the C=O bond of ketones or enals giving rise to an intermediate **II**, in which the four-membered P–Se–C–O ring breaks to generate an unstable α,β-unsaturated selenoketone or selenoenal **III** by loss of a molecule of PhP(Se)(O). Then, a further [2+2]-cycloaddition of a P=Se bond from $PhPSe_2$ (**I**) with the C=Se bond of intermediate **III** results in an intermediate **IVa**, existing in equilibrium in solution with **IVb**. The latter can readily be rearranged to intermediate **V**, followed by intramolecular cyclisation to afford the six-membered ring **VIa**, which is likely in equilibrium with its iso-structural **VIb** in solution at elevated temperature. Finally, we propose that both **VIa** and **VIb** can be undergo ring contraction by elimination of a molecule of selenium to give the more stable five-membered heterocycles **1**–**10**. Therefore, the form **A** is formed in products **1**, **2**, **4**, **5**, **7** and **10** consisting of two stereoisomers. Meanwhile, in the cases of products **3**, **6**, **8** and **9** two isomers **A** and **B** co-exist to give four stereoisomers. Unfortunately, we are not able to further separate or identify the different isomers.



Scheme 2 Synthesis of five-membered heterocycles **9** and **10** from



Scheme 3 Possible mechanism for the formation of five-membered heterocycles **1**–**10**

In conclusion, Woollins' reagent reacts with equimolar amount of α,β-unsaturated ketones in refluxing toluene giving a series of novel five-membered $C_3P(Se)Se$ heterocycles in good to excellent isolated yields.[24] Meanwhile, treating **WR** with an equivalent of aromatic conjugated enals under identical conditions resulted in the similar five-membered $C_3P(Se)Se$ heterocycles.[24] Two or four stereoisomers were observed by ^{31}P NMR and ^{77}Se NMR spectra.

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(18) Crystallographic Data for Compound **1a**: $C_{21}H_{17}PSe_2$, M = 458.24, monoclinic, space group $P2_{1/n}$, a = 9.948 (3), b = 16.347 (7), c = 11.640 (4) Å, β = 102.399 (8)°, U = 1848.7 (11) Å^3, Z = 4, μ = 1.646 mm^{-1}, 12616 reflections, 3627 unique (R_{int} = 0.038); R_1 = 0.044, wR_2 = 0.106.

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(24) Experimental Section: Unless otherwise stated, all reactions were carried out under an oxygen-free nitrogen atmosphere using pre-dried solvents and standard Schlenk techniques, subsequent chromatographic and workup procedures were performed in air. ^{1}H NMR (270 MHz), ^{13}C NMR (67.9 MHz), ^{31}P-{^{1}H} NMR (109 MHz) and ^{77}Se-{^{1}H} (51.4 MHz referenced to external Me_2Se) NMR spectra were recorded at 25 °C (unless stated otherwise) on a JEOL GSX 270 spectrometer. IR spectra were recorded as KBr pellets in the range of 4000–250 cm^{-1} on a Perkin–Elmer 2000 FTIR/ Raman spectrometer. Microanalysis was performed by the University of St-Andrews microanalysis service. Mass spectrometry was performed by the EPSRC National Mass Spectrometry Service Centre, Swansea and the University of St Andrews Mass Spectrometry Service. X-ray crystal data for **1**, were collected using a Rigaku SCXMIni Mercury CCD system. Intensity data were collected using ω steps accumulating area detector images spanning at least a hemisphere of reciprocal space. The data were corrected for Lorentz polarisation effects. Absorption effects were corrected on the basis of multiple equivalent reflections or by semi-empirical methods. Structures were solved by direct methods and refined by full-matrix least-squares against F^2 by using the program SHELXTL.[25] Hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealised geometries. The data (CCDC 855701) can be obtained free of charge via 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.

General Procedure for Synthesis of Compounds 1–8 from the Selenation of α,β-Unsaturated Ketones: A mixture of α,β-unsaturated ketone (1.0 mmol) and **WR** (0.54 g, 1.0 mmol) in anhyd toluene (20 mL) was refluxed for 7 h. Red suspension disappeared and a pale brown solution was formed along with small amount of grey elemental selenium precipitate. Upon cooling to r.t. and removing the unreacted solid by filtration the filtrate was dried in evaporator and purified by silica gel column (eluent: EtOAc–CH_2Cl_2, 1:1) to give compounds **1**–**8**.

Compound 1: yellow paste (425 mg) in 92% isolated yield. IR (KBr): 1599 (m, C=C), 1490 (m), 1434 (m), 1088 (m), 749 (s), 690 (s), 595 (m), 513 (m) cm^{-1}. A pair of stereoisomers was found in ca. 4:6 intensity ratio. ^{1}H NMR (CD_2Cl_2): δ = 8.21 (dd, 2 × 4 H, ArH), 7.01–7.59 (m, 2 × 10 H, ArH), 6.65 (dd, $J_{H,H}$ = 3.6 Hz, $J_{P,H}$ = 32.2 Hz, 1 H, HC=C), 6.57 (dd, $J_{H,H}$ = 3.6 Hz, $J_{P,H}$ = 32.2 Hz, 1 H, HC=C), 5.52 (dd, $J_{H,H}$ = 3.6 Hz, $J_{P,H}$ = 18.2 Hz, 1 H, HC), 5.09 (dd, $J_{H,H}$ = 3.6 Hz, $J_{P,H}$ = 18.2 Hz, 1 H, HC). ^{13}C NMR (CD_2Cl_2): δ = 142.3, 142.0, 141.8, 141.7, 136.1, 134.6, 134.1, 134.0, 133.1, 132.9, 132.8, 132.4, 132.1, 131.8, 131.7, 129.4, 129.0, 129.0, 128.8, 128.6, 128.5, 128.3, 128.2, 128.0, 127.9, 127.8, 127.3, 127.2, 125.4, 124.9, 71.6 (d, $J_{P,C}$ = 30.1 Hz), 65.8 (d, $J_{P,C}$ = 29.1 Hz). ^{31}P NMR (CD_2Cl_2): δ = 72.4 (s, J_{P-Se} = 346 Hz, $J_{P=Se}$ = 806 Hz), 71.4 (s, J_{P-Se} = 346 Hz, $J_{P=Se}$ = 786 Hz). ^{77}Se NMR (CD_2Cl_2): δ = 408.9 (d, J_{P-Se} = 346 Hz), 391.5 (d, J_{P-Se} = 346 Hz), –170.8 (d, $J_{P=Se}$ = 786 Hz), –187.5 (d, $J_{P=Se}$ = 806 Hz). MS (ESI$^+$): m/z = 483 [M + Na]$^+$. MS (CI$^+$): m/z = 461 [M + H]$^+$. HRMS (CI$^+$): m/z [M + H]$^+$ calcd for $C_{21}H_{18}PSe_2$: 460.9471; found: 460.9473.

Compound 2: yellowish milky solid (466 mg) in 95% isolated yield. IR (KBr): 1607 (m, C=C), 1510 (s, C=C), 1435 (m), 1303 (m), 1251 (s), 1177 (m), 1090 (m), 1030 (m), 831 (m), 746 (m), 688 (m), 596 (m), 521 (m) cm^{-1}. A pair of stereoisomers was found in ca. 4:6 intensity ratio. ^{1}H NMR (CD_2Cl_2): δ = 8.22 (dd, $J_{H,H}$ = 6.9 Hz, 2 × 4 H, ArH), 6.92–7.75 (m, 2 × 10 H, ArH), 6.65 (dd, 2 × 1 H, HC=C), 5.45 (dd, $J_{P,H}$ = 17.6 Hz, 2 × 1H, HC), 3.80 (s, 3 H, OMe), 3.69 (s, 3 H, OMe). ^{13}C NMR (CD_2Cl_2): δ = 141.8, 141.7, 141.4, 141.3, 136.2, 133.2, 133.0, 132.4 (d, $J_{P,C}$ = 3.1 Hz), 132.2 (d, $J_{P,C}$ = 3.1 Hz), 131.9, 131.7, 130.6, 130.5, 129.5, 129.4, 129.1, 129.0, 128.9, 128.7, 128.1, 127.9, 127.4, 127.3, 125.8, 125.3, 71.0 (d, $J_{P,C}$ = 31.1 Hz), 65.2 (d, $J_{P,C}$ = 29.1 Hz), 55.3. ^{31}P NMR (CD_2Cl_2): δ = 73.0 (s, J_{P-Se} = 336 Hz, $J_{P=Se}$ = 801 Hz), 71.6 (s, J_{P-Se} = 345 Hz, $J_{P=Se}$ = 784 Hz). ^{77}Se NMR (CD_2Cl_2): δ = 406.7 (d, J_{P-Se} = 336 Hz), 390.0 (d, J_{P-Se} = 345 Hz), –174.1 (d, $J_{P=Se}$ = 784 Hz), –188.2 (d, $J_{P=Se}$ = 801 Hz). MS (CI$^+$): m/z = 491 [M + H]$^+$. HRMS (CI$^+$): m/z [M + H]$^+$ calcd for $C_{22}H_{20}OPSe_2$: 490.9577; found: 490.9582.

Compound 3: pale yellow paste (320 mg) in 81% isolated yield. IR (KBr): 1555 (w, C=C), 1489 (m), 1433 (m), 1090 (m), 764 (m), 745 (m), 689 (s), 558 (m), 526 (m), 505 (m) cm^{-1}. Four stereoisomers were found in ca. 4:4:2:2 intensity ratio. ^{1}H NMR (CD_2Cl_2): δ = 7.98–8.19 (m, 4 × 2 H, ArH), 6.91–7.64 (m, 4 × 8 H, ArH), 6.38–6.63 (m, 4 × 1 H, CH), 5.92–6.19 (m, 4 × 1 H, CH), 2.32–2.34 (s, 4 × 3 H, Me). ^{13}C NMR (CD_2Cl_2): δ = 141.3, 141.1, 140.0, 139.9, 138.3, 138.2, 134.5, 134.4, 133.1, 132.9, 132.4, 132.3, 132.0, 131.7, 131.5, 129.4, 129.3, 129.1, 128.8, 128.7, 128.6, 128.4, 128.2, 128.1, 128.0, 127.9, 127.7, 125.3, 71.2, 70.8, 65.3, 64.9, 21.9, 21.2. ^{31}P NMR (CD_2Cl_2): δ = 75.6 (s, J_{P-Se} = 390 Hz, $J_{P=Se}$ = 765 Hz), 75.3 (s, J_{P-Se} = 336 Hz, $J_{P=Se}$ = 801 Hz), 74.7 (s, J_{P-Se} = 346 Hz, $J_{P=Se}$ = 782 Hz), 61.7 (s, J_{P-Se} = 390 Hz, $J_{P=Se}$ = 770 Hz). ^{77}Se NMR (CD_2Cl_2): δ = 449.7 (d, J_{P-Se} = 390 Hz), 443.9 (d, J_{P-Se} = 390 Hz), 421.4 (d, J_{P-Se} = 336 Hz), 405.5 (d, J_{P-Se} = 346 Hz), –111.7 (d, $J_{P=Se}$ = 770 Hz), –125.9 (d, $J_{P=Se}$ = 765 Hz), –156.7 (d, $J_{P=Se}$ = 782 Hz), –182.8 (d, $J_{P=Se}$ = 801 Hz). MS (EI$^+$): m/z = 398 [M]$^+$. HRMS (EI$^+$): m/z [M]$^+$ calcd for $C_{16}H_{15}P^{76}Se_2$: 389.9290; found: 389.99293.

Compound 4: orange solid (414 mg) in 84% isolated yield. IR (KBr): 1601 (m, C=C), 1505 (vs, C=C), 1434 (s), 1224 (s), 1158 (m), 1090 (m), 834 (s), 745 (s), 687 (m), 526 (m), 508 (s) cm^{-1}. A pair of stereoisomers was found in ca. 1:2 intensity ratio. ^{1}H NMR (CD_2Cl_2): δ = 8.14–8. 22 (d, $J_{H,H}$ = 7.2 Hz, 2 × 2 H, ArH), 6.74–7.69 (m, 2 × 11 H, ArH), 6.40–6.52 (d, 2 × 1 H, CH), 5.44–5.50 (d, 2 × 1 H, CH), 2.38 (s, 3 H, Me), 2.37 (s, 3 H, Me). ^{13}C NMR (CD_2Cl_2): δ = 164.6, 164.3, 161.0, 160.8, 140.0, 133.1, 132.9, 132.5, 132.3, 131.8, 131.6, 131.0, 130.3, 129.9, 129.7, 129.1, 128.8, 128.6, 128.5, 128.1, 127.9, 127.6, 127.2, 127.1, 124.1, 123.8, 70.9, 70.5, 65.1, 64.6, 21.1, 21.0. ^{31}P NMR (CD_2Cl_2): δ = 72.0 (s, J_{P-Se} = 340 Hz, $J_{P=Se}$ = 803 Hz), 70.7 (s, J_{P-Se} = 357 Hz, $J_{P=Se}$ = 789 Hz). ^{77}Se NMR (CD_2Cl_2): δ = 400.7 (d,

J_{P-Se} = 340 Hz), 386.5 (d, J_{P-Se} = 357 Hz), –177.8 (d, $J_{P=Se}$ = 789 Hz), –191.1 (d, $J_{P=Se}$ = 803 Hz). MS (CI$^+$): *m/z* = 493 [M + H]$^+$. MS (EI$^+$) *m/z* = 492 [M]$^+$. HRMS (EI$^+$): *m/z* [M]$^+$ calcd for $C_{22}H_{18}FP^{76}Se_2$: 483.9509; found: 483.9504.

Compound 5: yellow solid (403 mg) in 83% isolated yield. Two stereoisomers were found in ca. 1:2 intensity ratio. IR (KBr): 1598 (w, C=C), 1491 (m, C=C), 1434 (m, C=C), 1185 (w), 1165 (w), 1128 (w), 1088 (s), 939 (s), 764 (s), 745 (s), 688(vs), 630 (m), 595 (s), 506 (s, P=Se) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 7.47–7.63 (m, 2 × 2 H, ArH), 7.30–7.37 (m, 2 × 5 H, ArH), 7.12–7.21 (m, 2 × 4 H, ArH), 7.04–7.11 (m, 2 × 4 H, ArH), 6.93–6.96 (m, 2 × 2 H, ArH), 7.05 (d, *J* = 3.0 Hz, 1 H, CH), 6.95 (d, *J* = 3.0 Hz, 1 H, CH), 6.66 (dd, $^3J_{H,H}$ = 3.0 Hz, $^3J_{P,H}$ = 15.0 Hz, 1 H, CH), 6.36 (dd, $^3J_{H,H}$ = 3.0 Hz, $^2J_{P,H}$ = 32.0 Hz, 1 H, CH). ^{13}C NMR ($CDCl_3$): δ = 141.0, 136.0, 135.8, 133.1, 133.0, 132.6, 132.4, 132.0, 129.0, 128.8, 128.3, 128.2, 127.9, 127.8, 127.0, 125.2, 70.3 (d, $^1J_{P,C}$ = 29 Hz). ^{31}P NMR ($CDCl_3$): δ = 70.3 (s, J_{P-Se} = 338 Hz, $J_{P=Se}$ = 803 Hz), 69.9 (s, J_{P-Se} = 350 Hz, $J_{P=Se}$ = 782 Hz). ^{77}Se NMR ($CDCl_3$): δ = 374.0 (d, J_{P-Se} = 338 Hz), 354.9 (d, J_{P-Se} = 350 Hz), –170.7 (d, $J_{P=Se}$ = 782 Hz), –188.0 (d, $J_{P=Se}$ = 803 Hz). MS (ES$^+$): *m/z* = 507 [M + Na]$^+$. Anal. Calcd for $C_{23}H_{19}PSe_2$ (484.29): C, 57.04; H, 3.95. Found: C, 57.01; H, 3.99.

Compound 6: brown solid (340 mg) in 67% yield. ^{31}P NMR spectrum revealed four stereoisomers in ca. 4:2:1:2 intensity ratio. IR (KBr): 1691 (m, C=C), 1594 (m, C=C), 1518 (s, C=C), 1434 (m), 1343 (s), 1089 (m), 851 (s), 689 (s), 596 (m), 508 cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 7.54–8.30 (m, 4 × 10 H, thienyl-H, ArH), 7.00–7.32 (m, 2 H, thienyl-H), 6.75–6.93 (m, 4 × 1 H, =CH), 3.26–3.44 (m, 4 × 1 H, SeCH). ^{13}C NMR (CD_2Cl_2): δ = 150.4, 148.0, 147.7, 147.3, 143.5,142.1, 141.2, 139.2, 133.1, 133.0, 132.9, 132.7, 132.5, 132.0, 131.8, 129.1, 128.9, 128.8, 128.7, 128.6, 128.3, 128.1, 127.9, 127.8, 127.4, 127.1, 125.0, 124.6, 124.2, 123.9, 123.6, 67.6, 67.1, 61.8, 61.4, 41.1, 23.9. ^{31}P NMR (CD_2Cl_2): δ = 73.7 (s, J_{P-Se} = 331 Hz, $J_{P=Se}$ = 832 Hz), 71.8 (s, J_{P-Se} = 340 Hz, $J_{P=Se}$ = 796 Hz), 61.0 (s, J_{P-Se} = 366 Hz, $J_{P=Se}$ = 793 Hz), 54.1 (s, J_{P-Se} = 380 Hz, $J_{P=Se}$ = 782 Hz). ^{77}Se NMR (CD_2Cl_2): δ = 487.1 (d, J_{P-Se} = 381 Hz), 473.1 (d, J_{P-Se} = 365 Hz), 414.8 (d, J_{P-Se} = 329 Hz), 405.6 (d, J_{P-Se} = 341 Hz), –83.2 (d, $J_{P=Se}$ = 782 Hz), –161.5 (d, $J_{P=Se}$ = 793 Hz), –166.7 (d, $J_{P=Se}$ = 796 Hz), –190.8 (d, $J_{P=Se}$ = 832 Hz). MS (EI$^+$): *m/z* = 511 [M]$^+$. HRMS (EI$^+$): *m/z* [M]$^+$ calcd for $C_{19}H_{14}O_2NPS^{74}Se_2$: 498.8927; found: 498.8933.

Compound 7: dark red solid (250 mg)in 50% yield. ^{31}P NMR spectrum revealed two stereoisomers in ca. 3:1 intensity ratio. IR (KBr): 1634 (s, C=C), 1557 (m, C=C), 1539 (m, C=C), 1470 (s), 1435 (m), 1408 (m), 1220 (m), 1071 (m), 781 (m), 748 (m), 686 (s)cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 6.96–8.15 (m, 2 × 9 H, ArH), 6.41 (d, $J_{P,H}$ = 16.5 Hz, 1 H, CH), 6.40 (d, $J_{P,H}$ =16.5 Hz, 1 H, CH), 3.77–4.04 (m, 2 × 1 H, CH), 3.37 (s, 6 H, Me), 2.94 (s, 6 H, Me). ^{13}C NMR (CD_2Cl_2): δ = 142.6, 140.5, 138.2, 134.8, 132.7, 132.5, 132.3, 132.0, 131.4, 131.2, 130.2, 130.0, 128.8, 128.6, 127.2, 126.1, 61.1, 56.6, 37.1, 34.1. ^{31}P NMR (CD_2Cl_2): δ = 57.0 (s, J_{P-Se} = 333 Hz, $J_{P=Se}$ = 787 Hz), 56.1 (s, J_{P-Se} = 369 Hz, $J_{P=Se}$ = 785 Hz). ^{77}Se NMR (CD_2Cl_2): δ = 455.2 (d, J_{P-Se} = 369 Hz), 450.0 (d, J_{P-Se} = 333 Hz), –131.2 (d, $J_{P=Se}$ = 785 Hz), –131.6 (d, $J_{P=Se}$ = 787 Hz). MS (EI$^+$): *m/z* = 505 [M]$^+$. HRMS (EI$^+$): *m/z* [M]$^+$ calcd for $C_{17}H_{17}BrPSe_2$: 504.8612; found: 504.8615.

Compound 8: pale yellow solid (224 mg) in 48% yield. Multi-NMR spectrum revealed four stereoisomers in ca. 3:4:2:2 extensity ratio. IR (KBr): 1657 (s, C=C), 1432 (s), 1226 (m), 1089 (s), 819 (m), 699(vs), 595 (m), 507 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 8.22–7.01 (m, 4 × 9 H, thienyl-H + ArH), 6.65–6.94 (m, 4 × 2 H, thienyl-H), 5.65–5.75 (m, 4 × 1 H, =CH), 3.29–3.29 (m, 4 × 1 H, SeCH). ^{13}C NMR (CD_2Cl_2): δ = 144.2, 143.8, 143.6, 143.2, 138.9, 136.1, 135.2, 134.6, 133.7, 133.6, 133.0, 132.9, 132.7, 132.5, 132.4, 132.1, 131.7, 128.8, 128.3, 128.2, 128.0, 127.9, 127.3, 126.9, 125.2, 125.1, 123.7, 123.5, 44.5, 43.8, 43.3, 41.0. ^{31}P NMR (CD_2Cl_2): δ = 71.1 (s, J_{P-Se} = 336 Hz, $J_{P=Se}$ = 810 Hz), 69.1 (s, J_{P-Se} = 341 Hz, $J_{P=Se}$ = 792 Hz), 61.0 (s, J_{P-Se} = 377 Hz, $J_{P=Se}$ = 789 Hz), 60.5 (s, J_{P-Se} = 393 Hz, $J_{P=Se}$ = 777 Hz). ^{77}Se NMR (CD_2Cl_2): δ = 477.2 (d, J_{P-Se} = 377 Hz), 412.7 (d, J_{P-Se} = 341 Hz), 407.3 (d, J_{P-Se} = 336 Hz), 398.5 (d, J_{P-Se} = 393 Hz), –142.5 (d, $J_{P=Se}$ = 777 Hz), –166.4 (d, $J_{P=Se}$ = 789 Hz), –176.7 (d, $J_{P=Se}$ = 792 Hz), –203.3 (d, $J_{P=Se}$ = 810 Hz). MS (EI$^+$): *m/z* = 472 [M]$^+$. HRMS (EI$^+$): *m/z* [M]$^+$ calcd for $C_{17}H_{13}PS_2{}^{74}Se_2$: 459.8640; found: 459.8635.

General Procedure for Synthesis of Compounds 9 and 10 from the Selenation of Aromatic α,β-Unsaturated Enals: A red solution of aromatic enal (1.0 mmol) and **WR** (0.54 g, 1.0 mmol) in anhyd toluene (20 mL) was refluxed for 7 h. Red suspension disappeared and a pale brown solution along with small amount of grey elemental selenium precipitate was formed. Upon cooling to r.t. the mixture was dried in evaporator and the residue was purified by silica gel column (eluent: EtOAc–CH_2Cl_2, 1:5) to give compounds **9** and **10**.

Compound 9: reddish yellow paste (600 mg) in 79% isolated yield. ^{31}P NMR spectrum revealed a mixture of four stereoisomers in ca. 5:7:5:3 intensity ratio. IR (KBr): 1673 (s, C=C), 1491 (m), 1450 (m), 1434 (m), 1121 (m), 1088 (m), 961 (m), 764(vs), 693(vs), 591 (m), 511 (m)cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 7.92–8.11 (m, 2 H, ArH), 7.07–7.58 (m, 8 H, ArH), 6.84–6.96 (m, 1 H, CH), 6.58–6.66 (m, 1 H, CH), 6.11–6.16 (m, 1 H, CH). ^{13}C NMR (CD_2Cl_2): δ = 137.0, 136.7, 134.0, 133.5, 133.4, 132.4, 132.2, 132.0, 131.6, 130.7, 129.6, 129.5, 129.0, 128.9, 128.7, 128.6, 128.4, 128.2, 128.1, 127.9, 127.5, 126.6, 32.0. ^{31}P NMR (CD_2Cl_2): δ = 72.6 (s, J_{P-Se} = 326 Hz, $J_{P=Se}$ = 802 Hz), 72.1 (s, J_{P-Se} = 336 Hz, $J_{P=Se}$ = 784 Hz), 55.6 (s, J_{P-Se} = 383 Hz, $J_{P=Se}$ = 770 Hz), 55.5 (s, J_{P-Se} = 383 Hz, $J_{P=Se}$ = 767 Hz). MS (CI$^+$): *m/z* = 385 [M + H]$^+$. HRMS (CI$^+$): *m/z* [M + H]$^+$ calcd for $C_{15}H_{14}PSe_2$: 384.9160; found: 384.9159.

Compound 10: greyish yellow solid (230 mg) in 56% isolated yield. ^{31}P NMR spectrum revealed a pair of stereoisomers in ca. 1:2 intensity ratio. IR (KBr): 1597 (m, C=C), 1490 (s), 1460 (s), 1434 (m), 1244(vs), 1026 (m), 750 (s) cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ = 7.02–8.20 (m, 2 × 6 H, thienyl-H + ArH), 6.83–6.99 (m, 2 × 3 H, thienyl-H), 6.37–6.51 (m, 2 × 1 H, =CH), 5.38–5.44 (m, 2 × 1 H, PCH), 3.87 (s, 3 H, OMe), 3.80 (s, 3 H, OMe), 3.29–3.45 (m, 2 × 1 H, SeCH). ^{13}C NMR (CD_2Cl_2): δ = 157.4, 156.5, 148.0, 146.0, 133.7, 133.6, 132.0, 131.9, 131.7, 131.5, 129.7, 129.4, 129.3, 129.2, 129.1, 128.5, 128.3, 128.0, 127.9, 127.4, 127.3, 127.2, 127.0, 58.1, 57.6, 55.6, 55.5. ^{31}P NMR (CD_2Cl_2): δ = 71.9 (s, J_{P-Se} = 322 Hz, $J_{P=Se}$ = 798 Hz), 75.1 (s, J_{P-Se} = 315 Hz, $J_{P=Se}$ = 782 Hz). ^{77}Se NMR (CD_2Cl_2): δ = 410.8 (d, J_{P-Se} = 322 Hz), 381.6 (d, J_{P-Se} = 315 Hz), –91.4 (d, $J_{P=Se}$ = 782 Hz), –183.8 (d, $J_{P=Se}$ = 798 Hz). MS (CI$^+$): *m/z* = 415 [M + H]$^+$. HRMS (CI$^+$): *m/z* [M + H]$^+$ calcd for $C_{16}H_{16}OPSe_2$: 414.9265; found: 414.9264.

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