

# One-pot Approach to Organo Phosphorus-Chalcogen Macrocycles Incorporating Double OP(S)SC<sub>n</sub> or OP(Se)SeC<sub>n</sub> Scaffolds: A Synthetic and Structural Study

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**Abstract:** The development of new methodology for the preparation of functional macrocycles with practical applications is a fundamental important research area in macromolecular science. In this study, we report a new one-pot route for the synthesis of a series of macro-heterocycles by incorporating two phosphorus atoms and two chalcogen atoms and two oxygen atoms (double OP(S)SC<sub>n</sub> or OP(Se)SeC<sub>n</sub> scaffolds). The three-component condensation reactions of 2,4-diferrocenyl-1,3,2,4-diathiadiphosphetane 2,4-disulfide (**FeLR**, a ferrocene analogue of Lawesson's reagent) or 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide (**LR**, Lawesson's reagent), or 2,4-diphenyl-1,3,2,4-diselenadiphosphetane 2,4-diselenide (**WR**, Woollins' reagent), disodium alkenyl-diols, and dihalogenated alkanes are performed giving rise to soluble and air or moisture-stable macrocycles in good to excellent yields (up to 92%). This is the first systemically preparative and readily scalable example of one-pot ring opening/ring extending reaction of three-components to prepare phosphorus-chalcogen containing macrocycles. We also provide a systematic crystallographic study.

## Introduction

Macrocyclic compounds are attractive targets within areas including drug development, material science, and supramolecular chemistry by virtue of their widespread occurrence in nature and their intrinsic three-dimensional structure.<sup>[1]</sup> The classic and privileged macrocyclic molecules such as crown ethers, cryptands, spherands, cyclodextrins, and calixarenes have provided, for instance, powerful model systems in the study of the nature of various noncovalent bond interactions, molecular recognition, and self-assembly.<sup>[2]</sup> Functional macrocycles act also as platforms for the fabrication of sophisticated molecular architectures, sensing systems, optoelectronic devices and advanced materials.<sup>[2,3]</sup> In addition, tailor made macrocycles serve as molecular tools to enable the mechanistic study of organic reactions involving unstable species.<sup>[4]</sup> Furthermore, macrocycles containing a ring size of 12 atoms or more are capable of extremely potent biological activity and specificity. This can be clearly illustrated by the exquisite

biological activity of many macrocyclic natural products that has been harnessed by medicinal chemists to provide chemotherapy for a broad range of conditions. Current studies involving macrocyclic structures account for over 100 approved drugs covering examples of antibiotic, immunosuppressant and anticancer chemotherapeutics.<sup>[5]</sup> Nevertheless, the challenging problem of macrocyclization remains and provides impetus for the development of new technologies for the development of novel and functional macrocycles.<sup>[6]</sup> An important challenge in forming large ring molecules is the fact that it is often necessary to tailor reaction conditions to individual substrates,<sup>[7]</sup> which can render the generation of libraries impractical. In addition, the synthesis of the macrocycles containing bigger than ten-membered ring systems are very rarely explored.<sup>[8]</sup> Furthermore, the preparation of organo phosphorus-chalcogen heterocycles containing more than eight-membered rings with at least two chalcogen atoms are also limited.<sup>[9]</sup> The known methods to synthesize these heterocycles in general suffer from the use of highly toxic reagents with harsh reaction conditions, low yields or multi-step procedures.<sup>[10]</sup> The most well-known four-membered phosphorus-chalcogen rings are the Lawesson's (**LR**) and Woollins' reagent (**WR**), which have developed and exploited as a wide ranging applications in synthetic chemistry, for example, as efficient thionation and selenation reagents, respectively.<sup>[11,12]</sup> In particular, **WR** has successfully been applied as an efficient building block to construct a series of up to fifteen-membered selenophosphorus macrocycles with the P-Se-Se-P linkage,<sup>[13]</sup> and unique octaselenocyclododecane with four carbon atoms and eight selenium atoms in this fourteen-membered macrocycle.<sup>[14]</sup> Encouraged by our recently reported method on formation of phosphorus-selenium macrocycles rings from Woollins' reagent and diol precursors,<sup>[15]</sup> we are interested in generating a library of diverse phosphorus-chalcogen macrocycles based on this strategy. We report herein a highly efficient one-pot approach to construct a library of organo phosphorus-chalcogen macrocycles consisting of at least two phosphorus atoms and two chalcogen atoms and two oxygen atoms P<sub>2</sub>-X<sub>2</sub>-O<sub>2</sub> (X = S, Se) in the ring by applying four-membered ring **WR** or **LR** or a ferrocene analogue of Lawesson reagent, 2,4-diferrocenyl-1,3,2,4-diathiadiphosphetane 2,4-disulfide [FcP(μ-S)S]<sub>2</sub>, **FeLR**, as building block precursors. The new compounds were characterised spectroscopically and we also report nine single crystal X-ray structures.

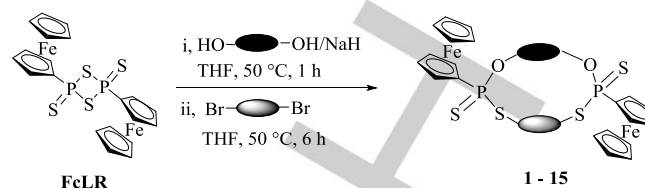
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## Results and Discussion

## Synthesis and Spectroscopic Characterization

Our group has reported an efficient route for the synthesis of phosphorus-selenium macrocycles including a series of unusual nine to fifteen-membered organoselenophosphorus macrocycles by means of **WR** reacting with disodium alkenyl-diols, followed by in-situ ring-closure reaction with appropriate dibromoalkanes.<sup>[15]</sup> We envisaged that this method has the potential to provide extremely efficient access to a range of macrocycles bearing double O-P(S)-S-C<sub>n</sub> or O-P(Se)-Se-C<sub>n</sub> scaffolds because the combinatorial variation of scaffold elements can lead to the generation of an unique scaffold from each macrocyclization process. Three reagents utilized to accomplish one-pot three-component reaction are: Lawesson's Reagent (**LR**), which is commercially available; a ferrocene analogue of Lawesson's Reagent, 2,4-diferrocenyl-1,3,2,4-diathiadiphosphetane 2,4-disulfide [FcP( $\mu$ -S)<sub>2</sub>] (**FcLR**), in which the preparation, spectroscopic characterisation and crystal structure of **FcLR** has been reported by our group;<sup>[16,17]</sup> and Woollins' Reagent (**WR**).<sup>[18]</sup> First, reacting **FcLR** with an equimolar amount of disodium alkane-bis(olate)s, which were obtained from di-alcohols and NaH, delivered the disodium bis(phenylphosphonodiselenoate)s, the latter were *in situ* converted into the corresponding nine- to fifteen-membered phosphorus-sulfur heterocycles **1 – 15** in moderate to excellent yields (43 to 92%) by further treatment with an equi-molar amount of various nucleophilic reagents, for instance, dibromides as depicted in Scheme 1 and Table 1. The reactions were carried out in tetrahydrofuran, which was chosen as the solvent because it provided good solubility properties for both small ring opening and macrocyclization processes. It was also found to be necessary to heat the reactions to 50°C to achieve the reaction completeness rapidly and the reactions were carried out under N<sub>2</sub> atmosphere for 7 h. In all the cases, insoluble (in water or normal organic solvent) side products which we were not able to identify were found resulting in the non-quantitative yields arising from the extensive formation of the possible linear polymers. The current reactions tolerate diverse di-alcohol substrates. Generally, the substituents on the di-alcohol chains have a large influence on the yield of the reaction, for example, with the increase of size of the branched substituent from hydrogen atom to *n*-butyl group, the product yield increased. The  $\alpha,\alpha'$ -dibromo-*o*-xyene was found to be preferable to achieve high yields in the current macrocyclization, compared to the  $\alpha,\alpha'$ -dibromo-*m*-xyene and  $\alpha,\alpha'$ -dibromo-*p*-xyene, for instance, the combination of propane-1,3-diol and  $\alpha,\alpha'$ -dibromo-*o*-xyene was found to give the product **5** with the highest yield. It is worth noting that in all cases two diastereomeric products were obtained

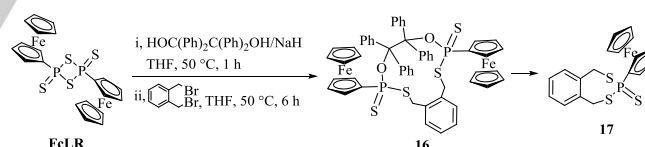
with low diastereoselectivity on the basis of <sup>31</sup>P NMR spectral data.



**Scheme 1.** Synthesis of macroheterocycles **1 – 15** (● and ○ groups defined in Table 1)

Macrocycles **1 – 15** are soluble in common polar organic solvents and are stable to air and moisture at ambient atmosphere for several months without any sign of the decomposition. All compounds **1 – 15** show the anticipated [M+H]<sup>+</sup> or [M+NH<sub>4</sub>]<sup>+</sup> peak in their mass spectra and satisfactory accurate mass measurements and appropriate isotopic distributions. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of compounds **1 – 15** display all the characteristic peaks of the ferrocene backbones (see Supporting Information). In their <sup>31</sup>P NMR spectra, sharp singlets attributable to phosphorus atoms of compounds **1 – 15** appear in the range of  $\delta = 92.4$  to 100.1 ppm as shown in Table 1.



Similarly, treating disodium 1,1,2,2-tetraphenylethane-1,2-di(olate) with **FcLR** and followed by  $\alpha,\alpha'$ -dibromo-*o*-xyene *in situ* in THF at 50°C gave rise to the expected twelve-membered macrocycle **16**. However, the macrocycle **16** was not stable in air atmosphere and seven-membered trithiophosphorus heterocycle **17** as yellow plate crystals was obtained by silica gel purification and crystallization. Stable seven-membered heterocycle **17** was obtained as the major product as illustrated in Scheme 2.

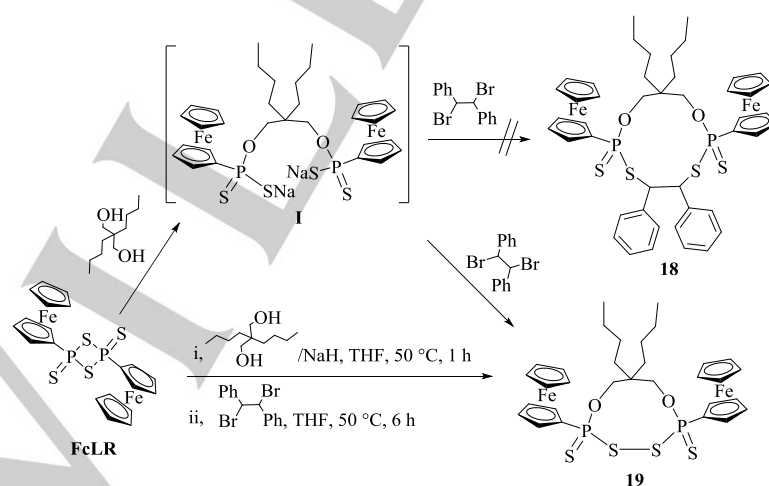


**Scheme 2.** Synthesis of phosphorus-sulfur macrocycle **16** and trithiophosphorus heterocycle **17**

Interestingly and in a similar vein, a similar reaction with the highly branched disodium 2,2-dibutylpropane-1,3-bis(olate) and the highly branched  $\alpha,\alpha'$ -dibromo-*o*-xyene led to formation of nine-membered macrocycle **19** (90% isolated yield) as the major product rather than the expected eleven-membered macrocycles **18** as shown in Scheme 3. We speculate that **19** was preferentially formed by intramolecular cyclization/oxidation of intermediate **I** in the presence of an equivalent of 1,2-di bromo-1,2-diphenylethane. The <sup>31</sup>P NMR spectrum of **19** exhibits a

**Table 1.** Groups defined, yields and  $^{31}\text{P}$  NMR spectral data of compounds **1** – **15**

Compound			Yield (%)	$^{31}\text{P}$ NMR ( $\delta$ , ppm)
<b>1</b>	$\text{CH}_2\text{CH}_2$	<i>o</i> - $\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2$	67	95.2 / 95.1
<b>2</b>	$\text{CH}_2\text{CH}_2$	<i>m</i> - $\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2$	49	99.9 / 99.7
<b>3</b>	$\text{CH}_2\text{CH}_2$	<i>p</i> - $\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2$	54	99.7 / 97.8
<b>4</b>	$\text{CH}_2\text{CH}_2\text{CH}_2$	<i>m</i> - $\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2$	43	99.0 / 98.9
<b>5</b>	$\text{CH}_2\text{CH}_2\text{CH}_2$	<i>o</i> - $\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2$	92	94.2 / 92.4
<b>6</b>	$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$	$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$	73	99.6 / 97.4
<b>7</b>	$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$	<i>o</i> - $\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2$	73	97.9 / 95.4
<b>8</b>	$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$	<i>m</i> - $\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2$	58	98.3 / 98.2
<b>9</b>	$\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$	<i>p</i> - $\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2$	67	98.3 / 98.2
<b>10</b>	$\text{CH}(\text{Ph})\text{CH}(\text{Ph})$	<i>o</i> - $\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2$	68	100.1 / 100.0
<b>11</b>	$\text{CH}(\text{Ph})\text{CH}(\text{Ph})$	<i>m</i> - $\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2$	55	100.1 / 99.7
<b>12</b>	$\text{CH}_2\text{C}(\text{tBu})_2\text{CH}_2$	<i>o</i> - $\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2$	60	94.1 / 93.7
<b>13</b>	$\text{CH}_2\text{C}(\text{tBu})_2\text{CH}_2$	<i>m</i> - $\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2$	71	98.7, 98.6
<b>14</b>	$\text{CH}_2\text{C}(\text{tBu})_2\text{CH}_2$	<i>p</i> - $\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2$	92	98.6 / 97.4
<b>15</b>	$\text{CH}_2\text{C}\equiv\text{CCH}_2$	<i>p</i> - $\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2$	52	100.5 / 100.4

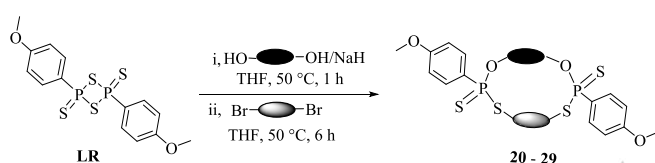
**Scheme 3.** Synthesis of phosphorus-sulfur heterocycle **19**

slightly broad singlet at  $\delta_{\text{P}} = 92.6$  ppm. Detailed NMR spectroscopic analysis reveals the relatively small coupling constant ( $^3J(\text{P},\text{P}) = 3.8$  Hz) between two four-coordinate phosphorus centers, supporting the presence of the P-S-S-P

group and being consistent with the analogous P-S-S-P system in the literature (cf.  $^3J(\text{P},\text{P}) = 4$  Hz).<sup>[19]</sup>

High efficiency for the synthesis of macrocycles **20** – **29** was remarkable when Lawesson's reagent reacted with bis-alcohols and bis-bromides under identical conditions to

give a series of new macrocycles **20** – **29** as depicted in Scheme 4 and Table 2. It was found to be necessary to heat the reactions to 50°C to achieve complete macrocyclization, and the reactions were carried out under N<sub>2</sub> atmosphere for 7 h. The products were obtained in good yields after flash chromatography. The highest yield was isolated when but-2-yne-1,4-diol was used indicating less conformational strain in macrocycle **29** compared to others. For eight examples **20**, **23** – **29**, diastereoisomers of the macrocyclic product were isolated, corresponding to two stereogenic P centers in the macrocycles; interestingly, for other two examples **21** and **22**, three diastereoisomers were isolated. We assume that two diastereoisomers were obtained from two stereogenic P centers present in the macrocycles, and the additional isomer was most likely result of one isomerization process involving two oxygen atoms and two sulfur atoms within the macrocyclic ring as shown in Figure 1. All of new compounds were characterized by standard analytical and spectroscopic techniques. The <sup>31</sup>P NMR spectra of **20** – **29** exhibit sharp singlets in the range of  $\delta = 88.2$  to 98.1 ppm.



**Scheme 4.** Synthesis of oxygen-phosphorus-sulfur macroheterocycles **20** – **29** (● and ○ groups defined in Table 2)

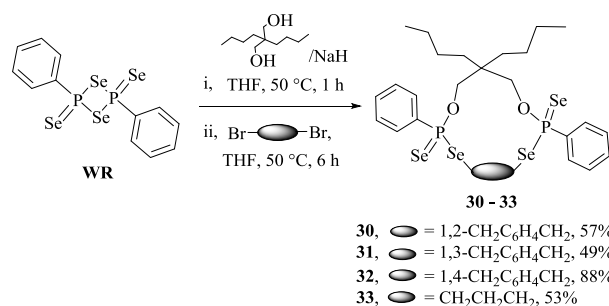
Now, we turn our attention to macrocycles containing multiple phosphorus, selenium and oxygen atoms. Rupture of the four-membered ring P<sub>2</sub>Se<sub>2</sub> in Woollins' reagent by an equimolar amount of disodium 1,2-diphenylethane-1,2-bis(olate) derived from 1,2-diphenylethane-1,2-diol and NaH led to disodium *O,O'*-(1,2-diphenylethane-1,2-diyl) bis(phenylphosphonodiselenoate), which was treated with an equivalent amount of  $\alpha,\alpha'$ -dibromoxyenes or dibromopropane at ambient temperature for 6 h resulting in the corresponding twelve- to fifteen-membered phosphorus-selenium macrocycles **30** – **33** in 49 – 88% isolated yields (Scheme 5). The macrocycles **30** – **33** are soluble in common polar organic solvents and are stable to air and moisture at ambient temperature for several months without any sign of the decomposition. All of new compounds were characterized by standard analytical and spectroscopic techniques. The <sup>31</sup>P NMR spectra of **30** – **33** exhibit sharp singlets in the range of  $\delta = 67.3$  to 79.9 ppm, which are accompanied by two sets of satellites for the endocyclic and exocyclic selenium atoms (<sup>1</sup>J(P,Se<sub>endo</sub>) = 440 to 465 Hz) and <sup>1</sup>J(P,Se<sub>exo</sub>) = 812 – 830 Hz), thus indicating the presence of single and double P=Se bonds in each compound. The results were further confirmed by the <sup>77</sup>Se NMR spectra of **30** – **33** that contain signals arising from exocyclic selenium in the range of  $\delta = 338.0$  to 480.8 ppm and endocyclic selenium atoms in the range of  $\delta = -104.8$  to -57.4 ppm with matching (<sup>1</sup>J(P,Se<sub>endo</sub>) and

<sup>1</sup>J(P,Se<sub>exo</sub>) coupling constants. These data are consistent with the values reported in similar structures in the literature.<sup>15</sup> Two phosphorus atoms in **30** – **33** are potentially stereogenic centres, thus, macrocycles **30** – **33** might be stereotopic with (*R,R*), (*S,S*), (*S,R*) and (*R,S*) stereoisomers possible. A pair of stereoisomers is observed with low diastereoselectivity on the basis of <sup>31</sup>P NMR of **30** – **33**.

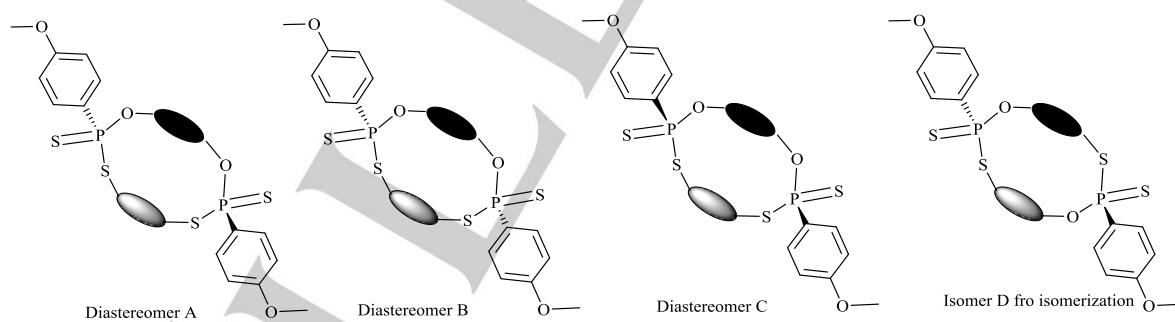
Woollins' reagent also reacted with an equimolar amount of disodium 1,2-diphenylethane-1,2-bis(olate) (which was derived from 1,2-diphenylethane-1,2-diol and NaH) leading to disodium *O,O'*-(1,2-diphenylethane-1,2-diyl) bis(phenylphosphonodiselenoate), the latter was treated with an equivalent amount of  $\alpha,\alpha'$ -dibromoxyenes at ambient temperature for 6 h resulting in the corresponding phosphorus-selenium macrocycles **34** – **36**. Unfortunately, these three macrocycles were not stable and eventually decomposed into a five-membered phosphorus-oxygen **38** in 75 – 80% isolated yield, respectively, however, for **34**, an additional seven-membered phosphorus-selenium heterocycle **37** was obtained in 69% isolated yield (Scheme 6). The synthesis and characterization of compounds **37** and **38** have been reported elsewhere.<sup>[20,21]</sup>

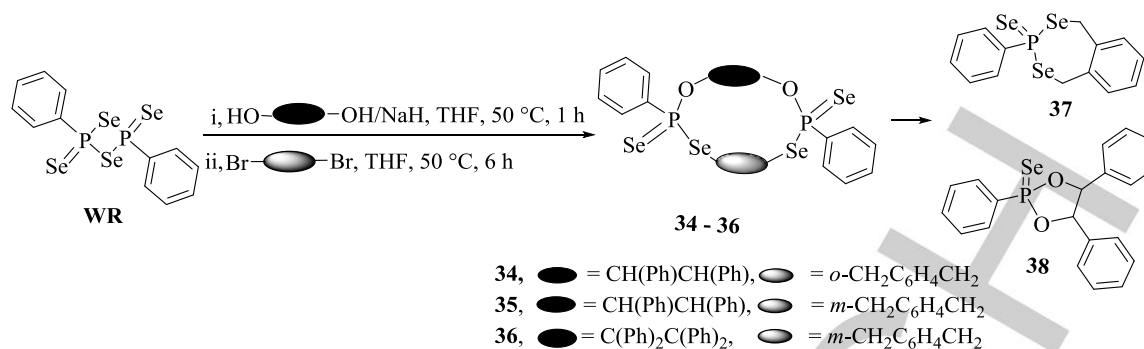
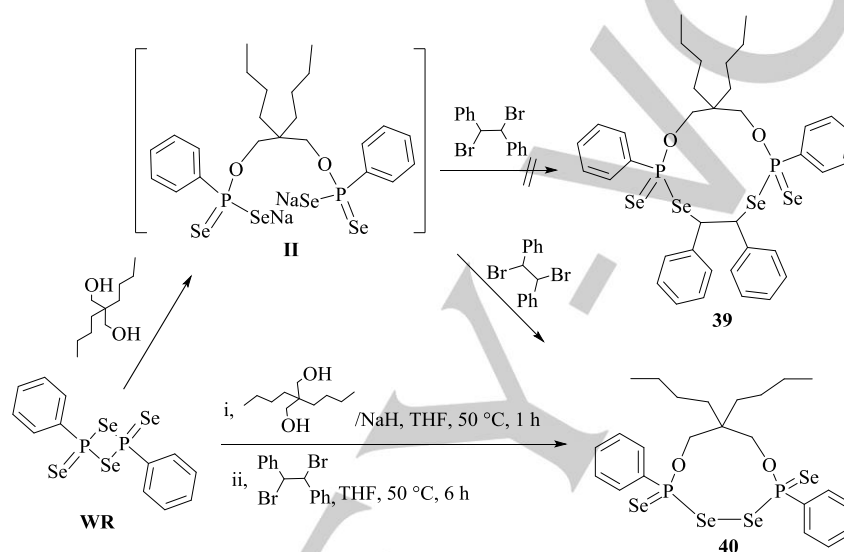
Similar to the reaction of **FcLR** with disodium 2,2-dibutylpropane-1,3-bis(olate) and  $\alpha,\alpha'$ -dibromo-*o*-xyene, Woollins' reagent reacted with disodium 2,2-dibutylpropane-1,3-bis(olate) and  $\alpha,\alpha'$ -dibromo-*o*-xyene under identical conditions gave selenium analogue nine-membered **40** incorporating with a P-Se-Se-P linkage in 77% isolated yield rather than the expected eleven-membered macrocycle **39** as illustrated in Scheme 7. The singlet at 67.3 ppm flanked by two sets of <sup>77</sup>Se satellites was observed in the <sup>31</sup>P NMR spectrum of **40**. The coupling constants were revealed to be <sup>1</sup>J(P,Se) = 465 Hz, and <sup>2</sup>J(P,Se) = 21.5 Hz based on simulation as an AA'X system (where X represents <sup>77</sup>Se and AA' are the magnetically in-equivalent phosphorus atoms in the isotopomer that gives rise to the satellite resonances), confirming the solution NMR spectra of **40** are consistent with the formation of a P-Se-Se-P linkage with chemically equivalent, but magnetically inequivalent phosphorus environments. The <sup>77</sup>Se NMR spectrum is comprised of two doublets centred at 439.5 and -57.5 ppm with <sup>1</sup>J(P,Se) = 465 Hz and <sup>1</sup>J(P,Se) = 812 Hz coupling constants. The detailed NMR spectroscopic analysis showing the relatively small coupling constant between phosphorus atoms (<sup>3</sup>J(P,P) = 3.7 Hz) further confirms the presence of the P-Se-Se-P group.<sup>[13]</sup> In contrast to the <sup>77</sup>Se satellites (natural abundance of 7.63%), the <sup>13</sup>C satellites in the <sup>31</sup>P NMR spectra can not be observed due to its very weak natural abundance (1.1%).



**Table 2.** Groups defined, yields and <sup>31</sup>P NMR spectral data of compounds **20 – 29**

Compound			Yield (%)	<sup>31</sup> P NMR (δ, ppm)
<b>20</b>	CH <sub>2</sub> CH <sub>2</sub>	CH <sub>2</sub> CH <sub>2</sub>	61	95.3, 91.6
<b>21</b>	CH <sub>2</sub> CH <sub>2</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	60	97.7, 97.5, 97.0
<b>22</b>	CH <sub>2</sub> CH <sub>2</sub>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	62	98.1, 97.6, 96.3
<b>23</b>	CH <sub>2</sub> CH <sub>2</sub>	<i>o</i> -CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	56	94.0, 93.1
<b>24</b>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	CH <sub>2</sub> CH <sub>2</sub>	61	93.8, 92.0
<b>25</b>	CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub>	<i>m</i> -CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	65	95.5, 95.4
<b>26</b>	CH <sub>2</sub> ( <sup>n</sup> Bu) <sub>2</sub> CH <sub>2</sub>	<i>o</i> -CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	62	90.6, 88.2
<b>27</b>	CH <sub>2</sub> ( <sup>n</sup> Bu) <sub>2</sub> CH <sub>2</sub>	<i>m</i> -CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	74	94.9, 94.8
<b>28</b>	CH <sub>2</sub> ( <sup>n</sup> Bu) <sub>2</sub> CH <sub>2</sub>	<i>p</i> -CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	67	94.0, 93.6
<b>29</b>	CH <sub>2</sub> C≡CCH <sub>2</sub>	<i>p</i> -CH <sub>2</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub>	81	96.6, 96.5

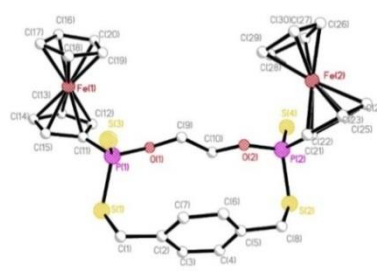
**Figure 1.** Possible three diastereomers in macrocycles **21** and **22** (diastereomers B and C should be the same product with identical <sup>31</sup>P chemical shift)

Scheme 6. Synthesis of phosphorus-selenium heterocycles **37** and **38**Scheme 7. Synthesis of phosphorus-selenium heterocycle **40**

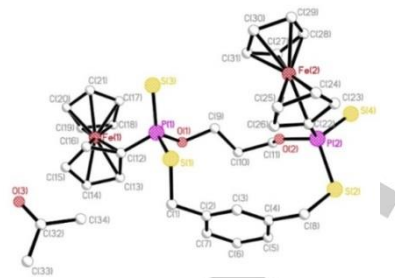
### Single Crystal X-ray Structures

Recrystallization from slow evaporation of acetone or dichloromethane solution of the compound in air at room temperature gave crystals of **3**, **4**, **5**, **10**, **11**, **26**, **29**, **30** and **40** suitable for X-ray diffraction studies. The results are shown in Figures 2 – 10 with crystallographic data listed in Tables S1 and S2 (see Supporting Information). All structures have a single molecule of the compound in the asymmetric unit, the exception being compound **4** in which was found to be co-crystallized with one molecule of acetone. The X-ray structures confirm that the twelve- to fifteen-membered rings have formed. In the solid state, **3** – **5** (Figures 2 – 4) adopt the highly ridged fourteen-membered ring conformations with two outside ferrocenyl rings pointing towards the top and bottom of the cavity and being located above the plane defined by the two phosphorus and two oxygen atoms, meanwhile two exocyclic sulfur atoms binding two phosphorus centres are crumpled in a *cis*-position relative to each other. In addition, all inward hetero-atoms (S, P, O) are in *zigzag* position, suggesting high strain exist in these fourteen-membered macrocyclic rings. The angles between the mean plane of two phosphorus atoms and two oxygen

atoms, and the phenyl ring are 43.3° in **3**, 20.1° in **4** and 26.1° in **5**. The P...P distances of 6.40 Å, 6.34 Å and 6.10 Å in **3** – **5**, respectively, falling in the ranges that has been observed in the P-Se containing macrocycles (4.97–6.97 Å).<sup>[15]</sup> The geometry around P(1) and P(2) is distorted tetrahedral S(3)–P(1)–S(1) and S(4)–P(2)–S(2): 114.38(15)° and 107.92(14)° in **3**, 105.94(10)° and 105.47(12)° in **4**, and 107.67(12)° and 107.70(12)° in **5**, being quite similar to those P-Se containing macrocycles.<sup>[15]</sup> Within **3** – **5**, the P–S single bond lengths are in the range of 2.087(3) to 2.097(4) Å and P=S double bonds in the range of 1.929(3) to 1.936(3) Å and are typical for the P(=S)S moiety.<sup>[20, 21]</sup>



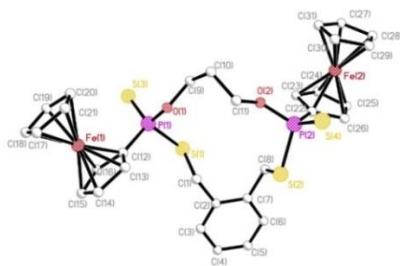
**Figure 2.** Single crystal X-ray structures of **3** (*SR isomer*) (hydrogen atoms omitted for clarity) Selected bond lengths (Å) and angles (°): S(1)-P(1) 2.093(4), S(2)-P(2) 2.088(4), S(3)-P(1) 1.935(4), S(4)-P(2) 1.928(4), P(1)-O(1) 1.605(7), P(2)-O(2) 1.599(6); S(1)-P(1)-S(3) 114.50(17), S(2)-P(2)-S(4) 108.04(16), S(1)-P(1)-O(1) 106.9(3), S(2)-P(2)-O(2) 107.3(3), S(3)-P(1)-O(1) 114.6(3), S(4)-P(2)-O(2) 116.6(3)



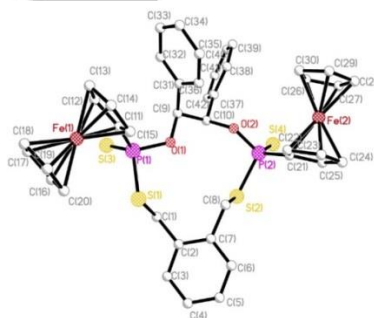
**Figure 3.** Single crystal X-ray structures of **4** (*RR isomer*) (hydrogen atoms omitted for clarity) Selected bond lengths (Å) and angles (°): S(1)-P(1) 2.093(3), S(2)-P(2) 2.087(4), S(3)-P(1) 1.930(4), S(4)-P(2) 1.936(4); S(1)-P(1)-S(3) 105.81(13), S(2)-P(2)-

S(4) 105.40(16), S(1)-P(1)-O(1) 107.8(3), S(2)-P(2)-O(2) 106.8(3), S(3)-P(1)-O(1) 117.5(3)

single bond lengths [2.077(2) to 2.1011(19) Å] and P=S double bonds [1.9217(18) to 1.9291(19) Å] are consistent with the typical values for the P(=S)S moiety.<sup>[22,23]</sup>

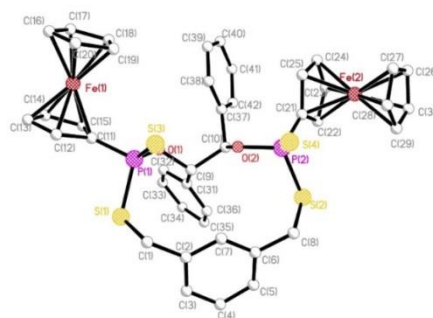


**Figure 4.** Single crystal X-ray structures of **5** (*SS isomer*) (hydrogen atoms omitted for clarity) Selected bond lengths (Å) and angles (°): [S(1)-P(1) 2.098(4), S(2)-P(2) 2.091(4), S(3)-P(1) 1.931(4), S(4)-P(2) 1.933(4), P(1)-O(1) 1.592(7), P(2)-O(2) 1.601(7); S(1)-P(1)-S(3) 107.70(16), S(2)-P(2)-S(4) 107.69(16), S(1)-P(1)-O(1) 105.3(3), S(2)-P(2)-O(2) 106.8(3)]



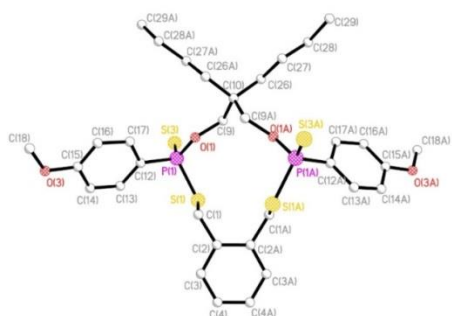
**Figure 5.** Single crystal X-ray structures of **10** (*SR isomer*) (hydrogen atoms omitted for clarity) Selected bond lengths (Å) and angles (°): S(1)-P(1) 2.083(2), S(2)-P(2) 2.077(2), S(3)-P(1) 1.929(3), S(4)-P(2) 1.926(3), P(1)-O(1) 1.608(4), P(2)-O(2) 1.621(4); S(1)-P(1)-S(3) 117.65(9), S(2)-P(2)-S(4) 107.45(10), S(1)-P(1)-O(1) 99.13(16), S(2)-P(2)-O(2) 106.37(15), S(3)-P(1)-O(1) 112.67(17), S(4)-P(2)-O(2) 117.31(17)

The structures of **10** and **11** as depicted in Figures 5 and 6 consist of similar frameworks. The thirteen- and fourteen-membered rings are also highly creased with two outside ferrocenyl rings lying in the same direction of the cavity and being above the plane defined by the two phosphorus and two oxygen atoms, meanwhile two exocyclic sulfur atoms which are directly attached to phosphorus centres are crinkled in a *trans*-orientation. All inward hetero-atoms (S, P, O) are in *zigzag* conformation, and two exocyclic phenyl rings lie in vertical orientation relative to the inward phenyl ring with slightly different angles (51.24° and 63.60° in **10**, 61.22° and 67.06° in **11**). Furthermore, the dihedral angles for two exocyclic phenyl rings are quite similar (52.79° in **10** and 52.65° in **11**). We think two exocyclic phenyl rings which were hanging on the cavity in the structures of **10** and **11** may cause the difference from the above structures of **3** – **5**. The P...P distances of 5.55 Å and 5.21 Å in **10** and **11** are found to be significantly shorter than that in **3** – **5**, suggesting a steric effect in these systems. The geometry around P(1) and P(2) is considerably closer to tetrahedral [(S(3)-P(1)-S(1) and S(4)-P(2)-S(2): 117.66(9)° and 107.45(9)° for **10**, and 113.48(8)° and 115.62(9)° for **11**]. In **10** and **11**, the P-S

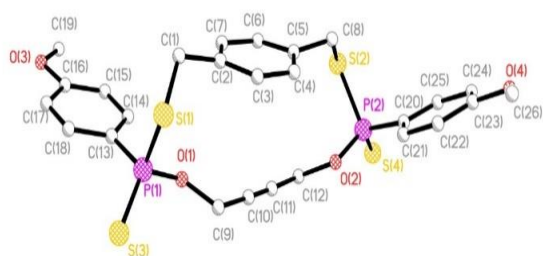


**Figure 6.** Single crystal X-ray structures of **11** (*SR isomer*) (hydrogen atoms omitted for clarity) Selected bond lengths (Å) and angles (°): S(1)-P(1) 2.099(3), S(2)-P(2) 2.096(3), S(3)-P(1) 1.920(2), S(4)-P(2) 1.932(2), P(1)-O(1) 1.601(5), P(2)-O(2) 1.602(6); S(1)-P(1)-S(3) 113.63(11), S(2)-P(2)-S(4) 115.52(13), S(1)-P(1)-O(1) 106.4(2), S(2)-P(2)-O(2) 107.0(2), S(3)-P(1)-O(1) 116.5(2), S(4)-P(2)-O(2) 107.9(2)

Within **26** and **29** (Figures 7 and 8), the frameworks are highly ridged thirteen- or sixteen-membered macrocycles with two aryl rings on phosphorus atoms and two exocyclic sulfur atoms pointing on opposite sides of the newly formed rings, suggesting that the two <sup>n</sup>Bu moieties present in **26** affect a lot for its conformation due to the steric effect. The structure of **26** is symmetric with the dihedral angle between the exocyclic aryl ring and the inserted aryl ring being 47.53°. However, the structure of **29** is asymmetric with the dihedral angles of two aryl rings and the inserted phenyl ring being 8.80° and 32.01°. The difference can also be found in the transannular S<sub>exo</sub>...S<sub>exo</sub> lengths (8.83 Å in **26** and 10.97 Å in **29**) and the interactional P...P bond distances (4.79 Å and 6.13 Å in compounds **5** and **9**), it is worth noting that these values are significantly bigger than that in **3** – **5**, **10** and **11**. The geometry around P(1) and P(2) is distorted tetrahedral (S(3)-P(1)-Se(1) and S(4)-P(2)-Se(2): 108.24(7)° for **26**, 106.89(13)° and 106.77(13)° for **29**). The P-S single bond lengths [2.075(16) to 2.090(3) Å] and P=Se double bonds [1.929(3) and 1.934(3) Å] are similar to those in **3** – **5**, **10** and **11**.

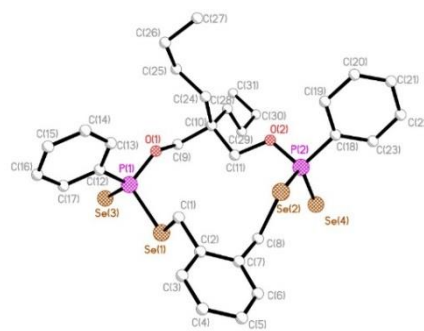


**Figure 7.** Single crystal X-ray structures of **26** (*SS isomer*) (hydrogen atoms omitted for clarity) Selected bond lengths (Å) and angles (°): S(1)-P(1) 2.0731(18), S(3)-P(1) 1.9332(19), P(1)-O(1) 1.598(4); S(1)-P(1)-O(1) 107.27(14), S(3)-P(1)-O(1) 115.88(14), P(1)-S(1)-C(1) 102.07(8), P(1)-O(1)-C(9) 121.3(3)



**Figure 8.** Single crystal X-ray structures of **29** (*SS isomer*) (hydrogen atoms omitted for clarity) Selected bond lengths (Å) and angles (°): S(1)-P(1) 2.090(5), S(3)-P(1) 1.930(5), P(1)-O(1) 1.599(8), P(2)-S(2) 2.082(5), S(4)-P(2) 1.934(5), P(2)-O(2) 1.602(8); S(3)-P(1)-S(1) 106.89(19), S(1)-P(1)-O(1) 106.7(4), S(3)-P(1)-O(1) 116.7(4), S(4)-P(2)-S(2) 106.77(19), S(2)-P(2)-O(2) 107.1(4), S(4)-P(2)-O(2) 116.8(4)

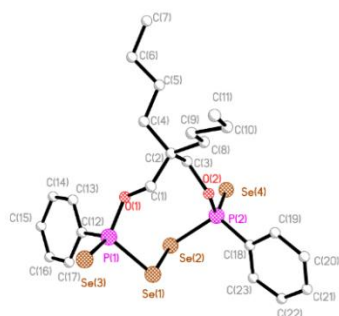
In contrast to **26**, the thirteen-membered macrocyclic structure of **30** (Figure 9) is asymmetric and highly creased with two phenyl rings attached to phosphorus atoms and two exocyclic selenium atoms lying on the same sides of the newly formed rings, and two <sup>n</sup>Bu moieties orientates toward the top and bottom of the newly formed macrocyclic ring. All inward hetero-atoms (Se, P, O) are in *zigzag* position. Two exocyclic phenyl rings are almost perpendicular relative to the inward phenyl ring with dihedral angles 75.15° and 89.15°. The transannular Se<sub>exo</sub>...Se<sub>exo</sub> length (8.15 Å) and the *i* P...P distance (6.31 Å) are in the range of similar structures<sup>15</sup> and significantly longer than those observed in the four-membered P<sub>2</sub>Se<sub>2</sub> ring system (3.1 Å) and six-membered P<sub>2</sub>Se<sub>4</sub> ring system (4.3 Å).<sup>24</sup> The P-Se single bonds [2.237(3) Å and 2.248(3) Å] and P=Se double bonds [2.085(3) Å and 2.083(3) Å] are similar to that in the similar heterocyclic structures incorporating with the P-Se-Se-P linkage.<sup>[13,15,25]</sup> The geometry around P(1) and P(2) is highly distorted tetrahedral [Se(3)-P(1)-Se(1) and Se(4)-P(2)-Se(2): 107.95(11)° and 114.59(12)°].



**Figure 9.** Single crystal X-ray structures of **30** (*SR isomer*) (hydrogen atoms omitted for clarity) Selected bond lengths (Å) and angles (°): Se(1)-P(1) 2.247(5), Se(3)-P(1) 2.079(6), P(1)-O(1) 1.593(10), Se(1)-Se(2) 2.350(4), Se(2)-P(2) 2.243(4), Se(4)-P(2) 2.081(6), P(2)-O(2) 1.587(13); Se(2)-Se(1)-P(1) 99.80(15), Se(1)-Se(2)-P(2) 102.81(16), Se(1)-P(1)-Se(3) 105.82(18), Se(1)-P(1)-O(1) 108.1(5), Se(3)-P(1)-O(1) 117.5(6), Se(2)-P(2)-Se(4) 102.88(19), Se(2)-P(2)-O(2) 108.7(5), Se(4)-P(2)-O(2) 118.0(5)

The structure of **40** reveals a difference motif to the above structures (Figure 10) with Se-Se bridge linker rather than Se-C<sub>n</sub>-Se bridge linker in the newly formed ring. The nine-membered framework is highly puckered with the two phenyl rings attached to phosphorus atoms and two exocyclic sulfur atoms and two <sup>n</sup>Bu moieties being on opposite sides of the newly formed heterocycle. The dihedral angle for the two exocyclic phenyl rings is 23.99°. The Se-Se bond distance [2.349(3) Å] is slightly longer than that in similar acyclic structures with the P-Se-Se-P linkage.<sup>[13,24]</sup> The P-Se single bonds [2.247(4) Å and 2.240(4) Å] and P=Se double bonds [2.077(5) Å and 2.084(5) Å] are consistent with that in the similar heterocyclic structures.<sup>[13,15,25]</sup> The Se-P-Se angles (Se(3)-P(1)-Se(1) and Se(4)-P(2)-Se(2): 105.90(17)° and 102.73(15)°) are highly twisted tetrahedral.





**Figure 10.** Single crystal X-ray structures of **40** (*RR* isomer) (hydrogen atoms omitted for clarity) Selected bond lengths (Å) and angles (°): Se(1)-P(1) 2.247(5), Se(3)-P(1) 2.079(6), P(1)-O(1) 1.593(10), Se(1)-Se(2) 2.350(4), Se(2)-P(2) 2.243(4), Se(4)-P(2) 2.081(6), P(2)-O(2) 1.587(13); Se(2)-Se(1)-P(1) 99.80(15), Se(1)-Se(2)-P(2) 102.81(16), Se(1)-P(1)-Se(3) 105.82(18), Se(1)-P(1)-O(1) 108.1(5), Se(3)-P(1)-O(1) 117.5(6), Se(2)-P(2)-Se(4) 102.88(19), Se(2)-P(2)-O(2) 108.7(5), Se(4)-P(2)-O(2) 118.0(5)

## Conclusions

A series of nine- to sixteen-membered macrocycles has been prepared by using an one-pot three-component condensation reactions of 2,4-diferrocenyl-1,3,2,4-diathiadiphosphetane 2,4-disulfide (**FcLR**, a ferrocene analogue of Lawesson's reagent) or 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide (**LR**, Lawesson's reagent), or 2,4-diphenyl-1,3,2,4-diselenadiphosphetane 2,4-diselenide (**WR**, Woollins' reagent), disodium alkenyl-diols, and dibromoalkanes. It was anticipated that this route would be a convenient pathway to synthesize novel macrocyclic compounds. The demonstrated versatility of synthesis and X-ray structures provides a general and systematic approach to prepare such large phosphorus-selenium heterocycles. This is the first systematically preparative and readily scalable example of one-pot ring opening/ring extending reaction of three-component to prepare phosphorus-chalcogen containing macrocycles. This method allows P-S or P-Se macrocycles to be easily available for further investigations into their chemistry and biological properties.

## Experimental Section

Unless otherwise stated, all reactions were carried out under on oxygen free nitrogen atmosphere using pre-dried solvents and standard Schlenk techniques, subsequent chromatographic and work up procedures were performed in air.  $^1\text{H}$  (400.1 MHz),  $^{13}\text{C}$  (100.6 MHz),  $^{31}\text{P}$ - $\{^1\text{H}\}$  (162.0 MHz) and  $^{77}\text{Se}$ - $\{^1\text{H}\}$  (51.4 MHz referenced to external  $\text{Me}_2\text{Se}$ ) NMR spectra were recorded at 25 °C (unless stated otherwise) on Bruker Advance II 400s and JEOL GSX 270. IR spectra were recorded as KBr pellets in the range of 4000-250  $\text{cm}^{-1}$  on a Perkin-Elmer 2000 FTIR/Raman spectrometer. Mass

spectrometry was performed by the EPSRC National Mass Spectrometry Service Centre, Swansea. X-ray crystal data for compounds **3**, **4**, **5**, **10**, **11**, **26**, **29**, **30** and **40** were collected using Rigaku SCXMini Mercury CCD system. Intensity data were collected using  $\omega$  steps accumulating area detector images spanning at least a hemisphere of reciprocal space. All data were corrected for Lorentz polarization 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.<sup>26</sup> Hydrogen atoms were assigned riding isotropic displacement parameters and constrained to idealized geometries. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) or from the Cambridge Crystallographic Data centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax (+44) 1223-336-033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk). CCDC 1439927-1439935.

**General procedure for synthesis of heterocycles 1 - 11.** A suspension of anhydrous diol (1.0 mmol) and sodium hydride (0.100 g, 60%, 2.5 mmol) in dry THF (60 mL) was heated at 50 °C for 1 h leading to a white suspension. Upon cooling to ambient temperature the suspension was added **FcLR** (0.56 g, 1.0 mmol) and the mixture was allowed to stir at room temperature for 2 h. Then, the appropriate dibromide (1.0 mmol) was added to the mixture and the suspension was continued heating at 50 °C for another 6 h giving a yellowish white suspension. Upon filtering to remove unreacted solid the filtrate was dried *in vacuo* and the residue was dissolved in dichloromethane (10 mL), after removing the salt by filtration the liquid solution was concentrated to *ca.* 2.0 mL and was loaded onto a silica gel column (50%/50% dichloromethane/hexane to 100% dichloromethane as eluent) to give the macrocycles **1 - 15**.

**3,8-Diferrocenyl-1,5,6,10-tetrahydrobenzo[*e*][1,10]dioxo[3,8]dithia[2,9]diphosphacyclododecine 3,8-disulfide (1).** Orange solid (0.482 g, 67%). Two diastereoisomers were found in *ca.* 2 : 1 intensity ratio. Selected IR (KBr,  $\text{cm}^{-1}$ ): 1448(m), 1411(m), 1385(m), 1239(m), 1181(s), 1106(m), 1066(m), 1024(s), 940(s), 822(m), 748(m), 668(s), 553(m), 486(s). Mass spectrum ( $\text{CI}^+$ ,  $m/z$ ), 725  $[\text{M}+\text{H}]^+$ . Accurate mass measurement [ $\text{CI}^+$ ,  $m/z$ ]: 724.9375  $[\text{M}+\text{H}]^+$ , calculated mass for  $\text{C}_{30}\text{H}_{30}\text{Fe}_2\text{O}_2\text{P}_2\text{S}_4\text{H}$ : 724.9375.

**4,9-Diferrocenyl-5,8-dioxa-3,10-dithia-4,9-diphospho-1(1,3)-benzenacycloundecaphane 4,9-disulfide (2).** Orange solid (0.354 g, 49%). Two diastereoisomers were found in *ca.* 1 : 1 intensity ratio. Selected IR (KBr,  $\text{cm}^{-1}$ ): 1443(m), 1411(m), 1181(s), 1106(m), 1068(m), 1024(vs), 949(s), 821(m), 779(m), 666(s), 549(m), 484(s). Mass spectrum ( $\text{CI}^+$ ,  $m/z$ ), 725  $[\text{M}+\text{H}]^+$ . Accurate mass measurement [ $\text{CI}^+$ ,  $m/z$ ]: 724.9381  $[\text{M}+\text{H}]^+$ , calculated mass for  $\text{C}_{30}\text{H}_{30}\text{Fe}_2\text{O}_2\text{P}_2\text{S}_4\text{H}$ : 724.9377.

**4,9-Diferrocenyl-5,8-dioxa-3,10-dithia-4,9-diphospho-1(1,4)-benzenacycloundecaphane 4,9-disulfide (3).** Orange solid (0.387 g, 54%). Two diastereoisomers were found in *ca.*

1 : 1 intensity ratio. Selected IR (KBr,  $\text{cm}^{-1}$ ): 1510(m), 1411(m), 1180(s), 1114(vs), 1105(m), 1024(vs), 957(s), 820(m), 774(m), 668(s), 554(s), 485(s). Mass spectrum ( $\text{CI}^+$ ,  $m/z$ ), 725 [ $\text{M}+\text{H}$ ] $^+$ . Accurate mass measurement [ $\text{CI}^+$ ,  $m/z$ ]: 724.9366 [ $\text{M}+\text{H}$ ] $^+$ , calculated mass for  $\text{C}_{30}\text{H}_{30}\text{Fe}_2\text{O}_2\text{P}_2\text{S}_4\text{H}$ : 724.9377.

**4,10-Diferrocenyl-5,9-dioxa-3,11-dithia-4,10-diphospha-1(1,3)-benzenacyclododecaphane 4,10-disulfide (4).** Golden foam (0.318 g, 43%). Two diastereoisomers were found in *ca.* 1 : 1 intensity ratio. Selected IR (KBr,  $\text{cm}^{-1}$ ): 1411(m), 1234(m), 1181(s), 1106(m), 1025(vs), 963(s), 822(s), 738(m), 704(m), 672(s), 551(s), 489(s). Mass spectrum ( $\text{CI}^+$ ,  $m/z$ ), 739 [ $\text{M}+\text{H}$ ] $^+$ . Accurate mass measurement [ $\text{CI}^+$ ,  $m/z$ ]: 738.9525 [ $\text{M}+\text{H}$ ] $^+$ , calculated mass for  $\text{C}_{31}\text{H}_{32}\text{Fe}_2\text{O}_2\text{P}_2\text{S}_4\text{H}$ : 738.9533.

**3,9-Diferrocenyl-1,6,7,11-tetrahydro-5H-benzo[*e*][1,10]dioxo[3,8]dithia[2,9]diphosphacyclotridecane 3,9-disulfide (5).** Orange solid (0.675 g, 92%). Two diastereoisomers were found in *ca.* 1 : 1 intensity ratio. Selected IR (KBr,  $\text{cm}^{-1}$ ): 1489(m), 1454(m), 1411(m), 1181(s), 1105(m), 1018(vs), 822(s), 698(vs), 667(s), 547(s), 494(vs), 492(s). Mass spectrum ( $\text{CI}^+$ ,  $m/z$ ), 739 [ $\text{M}+\text{H}$ ] $^+$ . Accurate mass measurement [ $\text{CI}^+$ ,  $m/z$ ]: 738.9522 [ $\text{M}+\text{H}$ ] $^+$ , calculated mass for  $\text{C}_{31}\text{H}_{32}\text{Fe}_2\text{O}_2\text{P}_2\text{S}_4\text{H}$ : 738.9533.

**2,9-Diferrocenyl-1,10-dioxa-3,8-dithia-2,9-diphosphacyclotetradecane 2,9-disulfide (6).** Golden foam (0.514 g, 73%). Two diastereoisomers were found in *ca.* 1 : 1 intensity ratio. Selected IR (KBr,  $\text{cm}^{-1}$ ): 1412(m), 1387(m), 1181(s), 1106(m), 1024(s), 1001(s), 822(s), 671(s), 557(s), 490(s). Mass spectrum ( $\text{CI}^+$ ,  $m/z$ ), 705 [ $\text{M}+\text{H}$ ] $^+$ . Accurate mass measurement [ $\text{CI}^+$ ,  $m/z$ ]: 704.9677 [ $\text{M}+\text{H}$ ] $^+$ , calculated mass for  $\text{C}_{28}\text{H}_{34}\text{Fe}_2\text{O}_2\text{P}_2\text{S}_4\text{H}$ : 704.9689.

**3,10-Diferrocenyl-1,5,6,7,8,12-hexahydrobenzo[*e*][1,10]dioxo[3,8]dithia[2,9]diphosphacyclotetradecane 3,10-disulfide (7).** Orange solid (0.551 g, 73%). Two diastereoisomers were found in *ca.* 1 : 3 intensity ratio. Selected IR (KBr,  $\text{cm}^{-1}$ ): 1491(m), 1453(m), 1412(m), 1182(s), 1106(m), 1023(vs), 820(s), 673(vs), 552(s), 493(vs). Mass spectrum ( $\text{CI}^+$ ,  $m/z$ ), 753 [ $\text{M}+\text{H}$ ] $^+$ . Accurate mass measurement [ $\text{CI}^+$ ,  $m/z$ ]: 752.9681 [ $\text{M}+\text{H}$ ] $^+$ , calculated mass for  $\text{C}_{32}\text{H}_{34}\text{Fe}_2\text{O}_2\text{P}_2\text{S}_4\text{H}$ : 752.9690.

**4,11-Diferrocenyl-5,10-dioxa-3,12-dithia-4,11-diphospha-1(1,3)-benzenacyclotridecaphane 4,11-disulfide (8).** Golden foam (0.436 g, 58%). Two diastereoisomers were found in *ca.* 3 : 2 intensity ratio. Selected IR (KBr,  $\text{cm}^{-1}$ ): 1411(m), 1181(s), 1106(m), 1025(s), 1000(s), 821(s), 706(m), 669(s), 549(s), 489(s). Mass spectrum ( $\text{CI}^+$ ,  $m/z$ ), 753 [ $\text{M}+\text{H}$ ] $^+$ . Accurate mass measurement [ $\text{CI}^+$ ,  $m/z$ ]: 752.9690 [ $\text{M}+\text{H}$ ] $^+$ , calculated mass for  $\text{C}_{32}\text{H}_{34}\text{Fe}_2\text{O}_2\text{P}_2\text{S}_4\text{H}$ : 752.9690.

**4,11-Diferrocenyl-5,10-dioxa-3,12-dithia-4,11-diphospha-1(1,4)-benzenacyclotridecaphane 4,11-disulfide (9).** Orange solid (0.505 g, 67%). Two diastereoisomers were found in *ca.* 2 : 1 intensity ratio. Selected IR (KBr,  $\text{cm}^{-1}$ ): 1510(m), 1411(m), 1240(m), 1181(s), 1105(m), 1024(vs),

1005(vs), 820(s), 670(s), 549(s), 490(s). Mass spectrum ( $\text{CI}^+$ ,  $m/z$ ), 753 [ $\text{M}+\text{H}$ ] $^+$ . Accurate mass measurement [ $\text{CI}^+$ ,  $m/z$ ]: 752.9688 [ $\text{M}+\text{H}$ ] $^+$ , calculated mass for  $\text{C}_{32}\text{H}_{34}\text{Fe}_2\text{O}_2\text{P}_2\text{S}_4\text{H}$ : 752.9690.

**3,8-Dimethyl-5,6-diphenyl-1,5,6,10-tetrahydrobenzo[*e*][1,10]dioxo[3,8]dithia[2,9]diphosphacyclododecane 3,8-disulfide (10).** Orange solid (0.596 g, 68%). Two diastereoisomers were found in *ca.* 4 : 5 intensity ratio. Selected IR (KBr,  $\text{cm}^{-1}$ ): 1490(m), 1452(s), 1411(m), 1182(s), 1106(m), 1025(s), 982(s), 821(m), 762(m), 698(vs), 543(m), 485(s). Mass spectrum ( $\text{CI}^+$ ,  $m/z$ ), 877 [ $\text{M}+\text{H}$ ] $^+$ . Accurate mass measurement [ $\text{CI}^+$ ,  $m/z$ ]: 877.0003 [ $\text{M}+\text{H}$ ] $^+$ , calculated mass for  $\text{C}_{42}\text{H}_{38}\text{Fe}_2\text{O}_2\text{P}_2\text{S}_4\text{H}$ : 876.9999.

**4,9-Diferrocenyl-6,7-diphenyl-5,8-dioxa-3,10-dithia-4,9-diphospha-1(1,3)-benzenacycloundecaphane 4,9-disulfide (11).** Pale yellow solid (0.481 g, 55%). Two diastereoisomers were found in *ca.* 3 : 2 intensity ratio. Selected IR (KBr,  $\text{cm}^{-1}$ ): 1487(m), 1453(m), 1413(m), 1181(s), 1106(m), 1027(s), 975(s), 892(m), 821(m), 702(vs), 546(m), 485(s). Mass spectrum ( $\text{CI}^+$ ,  $m/z$ ), 877 [ $\text{M}+\text{H}$ ] $^+$ . Accurate mass measurement [ $\text{CI}^+$ ,  $m/z$ ]: 877.0007 [ $\text{M}+\text{H}$ ] $^+$ , calculated mass for  $\text{C}_{42}\text{H}_{38}\text{Fe}_2\text{O}_2\text{P}_2\text{S}_4\text{H}$ : 877.0001.

**6,6-Dibutyl-3,9-diferrocenyl-1,6,7,11-tetrahydro-5H-benzo[*e*][1,10]dioxo[3,8]dithia[2,9]diphosphacyclotridecane 3,9-disulfide (12).** A white suspension of  $\text{HOCH}_2\text{C}(\text{tBu})_2\text{CH}_2\text{OH}$  (0.188 g, 1.0 mmol) and NaH (0.10 g, 60%, 2.5 mmol) in THF (60 mL) was heated at 50 °C for 2 h. After cooling to room temperature, **FcLR** (0.56 g, 1.0 mmol) was added; the mixture was stirred at room temperature for 1 h. Then, 1,2-xylylenedibromide (0.264 g, 1.0 mmol) was added to the above mixture, the mixture was heated again at 50 °C for another 6 h. Upon filtering to remove unreacted solid the filtrate was dried *in vacuo* and the residue was dissolved in dichloromethane (10 mL), after removing the salt by filtration the liquid solution was concentrated to *ca.* 2.0 mL and was loaded onto a silica gel column (50%/50% dichloromethane/hexane as eluent) to give the titled compound **12** as yellow solid (0.465 g, 55%). Two diastereoisomers were found in *ca.* 1 : 1 intensity ratio. Selected IR (KBr,  $\text{cm}^{-1}$ ): 1466(m), 1421(m), 1384(m), 1307(m), 1181(s), 1107(m), 1024(s), 988(s), 823(s), 766(m), 704(m), 681(s), 545(s), 494(s), 449(m). Mass spectrum ( $\text{CI}^+$ ,  $m/z$ ), 851 [ $\text{M}+\text{H}$ ] $^+$ . Accurate mass measurement [ $\text{CI}^+$ ,  $m/z$ ]: 851.0773 [ $\text{M}+\text{H}$ ] $^+$ , calculated mass for  $\text{C}_{39}\text{H}_{48}\text{Fe}_2\text{O}_2\text{PS}_4\text{H}$ : 851.0784.

**7,7-Dibutyl-4,10-diferrocenyl-5,9-dioxa-3,11-dithia-4,10-diphospha-1(1,3)-benzenacyclododecaphane 4,10-disulfide (13).** A white suspension of  $\text{HOCH}_2\text{C}(\text{tBu})_2\text{CH}_2\text{OH}$  (0.188 g, 1.0 mmol) and NaH (0.10 g, 60%, 2.5 mmol) in THF (60 mL) was heated at 50 °C for 2 h. After cooling to room temperature, **FcLR** (0.56 g, 1.0 mmol) was added; the mixture was stirred at room temperature for 1 h. Then, 1,3-xylylenedibromide (0.264 g, 1.0 mmol) was added to the above mixture, the mixture was heated again at 50 °C for another 6 h. Upon filtering to remove unreacted solid the filtrate was dried *in vacuo* and the residue was dissolved in

dichloromethane (10 mL), after removing the salt by filtration the liquid solution was concentrated to *ca.* 2.0 mL and was loaded onto a silica gel column (50%/50% dichloromethane/hexane as eluent) to give the titled compound **13** as yellow solid (0.605 g, 71%). Two diastereoisomers were found in *ca.* 1 : 2 intensity ratio. Selected IR (KBr,  $\text{cm}^{-1}$ ): 1462(m), 1411(m), 1370(m), 1232(m), 1182(s), 1106(m), 1025(s), 1001(s), 823(s), 705(m), 679(s), 550(s), 485(s), 447(m). Mass spectrum ( $\text{CI}^+$ ,  $m/z$ ), 851  $[\text{M}+\text{H}]^+$ . Accurate mass measurement [ $\text{CI}^+$ ,  $m/z$ ]: 851.0796  $[\text{M}+\text{H}]^+$ , calculated mass for  $\text{C}_{39}\text{H}_{48}\text{Fe}_2\text{O}_2\text{PS}_4\text{H}$ : 851.0784.

#### 7,7-Dibutyl-4,10-diferrocenyl-5,9-dioxa-3,11-dithia-4,10-diphospha-1(1,4)-benzenacyclododecaphane 4,10-disulfide (**14**).

A white suspension of  $\text{HOCH}_2\text{C}(\text{nBu})_2\text{CH}_2\text{OH}$  (0.188 g, 1.0 mmol) and NaH (0.10 g, 60%, 2.5 mmol) in THF (60 mL) was heated at 50 °C for 2 h. After cooling to room temperature, **FcLR** (0.56 g, 1.0 mmol) was added; the mixture was stirred at room temperature for 1 h. Then, 1,4-xylylenedibromide (0.264 g, 1.0 mmol) was added to the above mixture, the mixture was heated again at 50 °C for another 6 h. Upon filtering to remove unreacted solid the filtrate was dried *in vacuo* and the residue was dissolved in dichloromethane (10 mL), after removing the salt by filtration the liquid solution was concentrated to *ca.* 2.0 mL and was loaded onto a silica gel column (50%/50% dichloromethane/hexane as eluent) to give the titled compound **14** as yellow powder (0.784 g, 92%). Two diastereoisomers were found in *ca.* 2 : 1 intensity ratio. Selected IR (KBr,  $\text{cm}^{-1}$ ): 1462(m), 1411(m), 1242(m), 1182(s), 1105(m), 1024(s), 988(s), 835(s), 821(s), 678(vs), 553(s), 484(s), 445(m). Mass spectrum ( $\text{CI}^+$ ,  $m/z$ ), 851  $[\text{M}+\text{H}]^+$  or 868  $[\text{M}+\text{NH}_4]^+$ . Accurate mass measurement [ $\text{CI}^+$ ,  $m/z$ ]: 851.0800  $[\text{M}+\text{H}]^+$  or 868.1058  $[\text{M}+\text{NH}_4]^+$ , calculated mass for  $\text{C}_{39}\text{H}_{48}\text{O}_2\text{Fe}_2\text{PS}_4\text{H}$ : 851.0784 or for  $\text{C}_{39}\text{H}_{48}\text{O}_2\text{Fe}_2\text{PS}_4\text{NH}_4$ : 868.1050.

#### 4,11-Diferrocenyl-5,10-dioxa-3,12-dithia-4,11-diphospha-1(1,4)-benzenacyclotridecaphan-7-yne 4,11-disulfide (**15**).

A white suspension of  $\text{HOCH}_2\text{C}\equiv\text{CCH}_2\text{OH}$  (0.086 g, 1.0 mmol) and NaH (0.10 g, 60%, 2.5 mmol) in THF (60 mL) was heated at 50 °C for 2 h. After cooling to room temperature, **FcLR** (0.56 g, 1.0 mmol) was added; the mixture was stirred at room temperature for 1 h. Then, 1,4-xylylenedibromide (0.264 g, 1.0 mmol) was added to the above mixture, the mixture was heated again at 50 °C for another 6 h. Upon filtering to remove unreacted solid the filtrate was dried *in vacuo* and the residue was dissolved in dichloromethane (10 mL), after removing the salt by filtration the liquid solution was concentrated to *ca.* 2.0 mL and was loaded onto a silica gel column (dichloromethane as eluent) to give the titled compound **15** as golden foam (0.375 g, 52%). Two diastereoisomers were found in *ca.* 1 : 1 intensity ratio. Selected IR (KBr,  $\text{cm}^{-1}$ ): 1508(m), 1411(m), 1363(m), 1239(m), 1181(s), 1105(m), 1019(s), 1002(s), 971(s), 821(s), 676(vs), 554(s), 489(vs). Mass spectrum ( $\text{CI}^+$ ,  $m/z$ ), 749  $[\text{M}+\text{H}]^+$ . Accurate mass measurement [ $\text{CI}^+$ ,  $m/z$ ]: 748.9377  $[\text{M}+\text{H}]^+$ , calculated mass for  $\text{C}_{32}\text{H}_{30}\text{Fe}_2\text{O}_2\text{P}_2\text{S}_4\text{H}$ : 748.9381.

**Synthesis of heterocycles 16 and 17.** A suspension of benzopinacol (0.366 g, 1.0 mmol) and sodium hydride (0.100 g, 60%, 2.5 mmol) in dry THF (60 mL) was heated at 50 °C for 1 h leading to a white suspension. Upon cooling to ambient temperature the suspension was added **FcLR** (0.56 g, 1.0 mmol) and the mixture was allowed to stir at room temperature for 2 h. Then, 1,2-xylylenedibromide (0.264 g, 1.0 mmol) was added to the mixture and the suspension was continued heating at 50 °C for another 6 h giving a yellowish suspension. Upon filtering to remove unreacted solid the filtrate was dried *in vacuo* and the residue was dissolved in dichloromethane (10 mL), after removing the salt by filtration the liquid solution was concentrated to *ca.* 2.0 mL and was loaded onto a silica gel column (dichloromethane as eluent) to give the titled compound **16**. Crystallisation from slow evaporation of acetone solution of **16** in air at room temperature gave the crystals of **17**.

#### 3,8-Diferrocenyl-5,5,6,6-tetraphenyl-1,5,6,10-tetrahydrobenzo[e][1,10]dioxo[3,8]dithia[2,9]-diphosphacyclododecane 3,8-disulfide (**16**).

Dark green paste (0.395 g, 39%). Two diastereoisomers were found in *ca.* 1 : 1 intensity ratio. Selected IR (KBr,  $\text{cm}^{-1}$ ): 1657(s), 1598(m), 1493(m), 1448(m), 1316(m), 1277(s), 1181(m), 1027(m), 979(m), 825(m), 744(m), 701(vs), 638(m), 556(s), 492(s). Mass spectrum ( $\text{CI}^+$ ,  $m/z$ ), 1029  $[\text{M}+\text{H}]^+$ . Accurate mass measurement [ $\text{CI}^+$ ,  $m/z$ ]: 1029.0615  $[\text{M}+\text{H}]^+$ , calculated mass for  $\text{C}_{54}\text{H}_{46}\text{Fe}_2\text{O}_2\text{P}_2\text{S}_4\text{H}$ : 1029.0633.

#### 3-Ferrocenyl-1,5-

#### dihydrobenzo[e][1,3,2]dithiaphosphepine 3-sulfide (**17**).

Slightly yellow crystals (0.085 g, 20%). Selected IR (KBr,  $\text{cm}^{-1}$ ): 1491(m), 1440(m), 1409(m), 1253(m), 1216(m), 1203(m), 1160(s), 1020(s), 828(m), 766(s), 671(m), 621(m), 564(s), 545(vs), 483(vs), 450(m). Mass spectrum ( $\text{EI}^+$ ,  $m/z$ ), 416  $[\text{M}]^+$ . Accurate mass measurement [ $\text{EI}^+$ ,  $m/z$ ]: 415.9568  $[\text{M}]^+$ , calculated mass for  $\text{C}_{18}\text{H}_{17}\text{FePS}_3$ : 415.9574.

#### 8,8-Dibutyl-2,5-diferrocenyl-1,6,3,4,2,5-

#### dioxadithiadiphosphonane 2,5-disulfide (**19**).

A white suspension of  $\text{HOCH}_2\text{C}(\text{nBu})_2\text{CH}_2\text{OH}$  (0.329 g, 1.75 mmol) and NaH (0.16 g, 60%, 4.0 mmol) in THF (60 mL) was heated at 50 °C for 2 h. After cooling to room temperature, **FcLR** (0.98 g, 1.75 mmol) was added; the mixture was stirred at room temperature for 1 h. Then, *meso*-1,2-dibromide-1,2-phenylethane (0.595 g, 1.75 mmol) was added to the above mixture, the mixture was heated again at 50 °C for another 6 h. Upon filtering to remove unreacted solid the filtrate was dried *in vacuo* and the residue was dissolved in dichloromethane (10 mL), after removing the salt by filtration the liquid solution was concentrated to *ca.* 2.0 mL and was loaded onto a silica gel column (50%/50% dichloromethane/hexane as eluent) to give the titled compound **19** as a dark yellow solid (0.672 g, 90%). M.p. 164-166 °C. Selected IR (KBr,  $\text{cm}^{-1}$ ): 1494(m), 1453(s), 1377(m), 1261(m), 1137(m), 1023(m), 803(m), 762(s), 691(vs), 600(vs), 551(m), 487(m). Mass spectrum ( $\text{EI}^+$ ,  $m/z$ ), 746  $[\text{M}]^+$ . Accurate mass measurement [ $\text{EI}^+$ ,  $m/z$ ]: 746.0080  $[\text{M}]^+$ , calculated mass for  $\text{C}_{31}\text{H}_{40}\text{Fe}_2\text{O}_2\text{P}_2\text{S}_4$ : 746.0085.



**General procedure for synthesis of heterocycles 20 – 25.**

A suspension of anhydrous diol (1.0 mmol) and sodium hydride (0.100 g, 60%, 2.5 mmol) in dry THF (60 mL) was heated at 50 °C for 1 h leading to a white suspension. Upon cooling to ambient temperature the suspension was added **LR** (0.404 g, 1.0 mmol) and the mixture was allowed to stir at room temperature for 2 h. Then, the appropriate dibromide (1.0 mmol) was added to the mixture and the suspension was continued heating at 50 °C for another 6 h giving a yellowish white suspension. Upon filtering to remove unreacted solid the filtrate was dried *in vacuo* and the residue was dissolved in dichloromethane (10 mL), after removing the salt by filtration the liquid solution was concentrated to *ca.* 2.0 mL and was loaded onto a silica gel column (50%/50% dichloromethane/hexane to 100% dichloromethane as eluent) to give the macrocycles **20 – 25**.

**2,7-Bis(4-methoxyphenyl)-1,8,3,6,2,7-dioxadithiadiphospecane 2,7-disulfide (20).** Colorless paste (0.298 g, 61%). Two diastereoisomers were found in *ca.* 4 : 5 intensity ratio. Selected IR (KBr, cm<sup>-1</sup>): 1594(vs), 1499(s), 1458(m), 1408(m), 1296(m), 1259(s), 1180(m), 1113(s), 1024(s), 922(m), 830(m), 803(m), 686(s), 618(s), 538(s). Mass spectrum (CI<sup>+</sup>, m/z), 493 [M+H]<sup>+</sup>. Accurate mass measurement [CI<sup>+</sup>, m/z]: 492.9940 [M+H]<sup>+</sup>, calculated mass for C<sub>18</sub>H<sub>22</sub>O<sub>4</sub>P<sub>2</sub>S<sub>4</sub>H: 492.9949.

**2,8-Bis(4-methoxyphenyl)-1,9-dioxa-3,7-dithia-2,8-diphosphacycloundecane 2,8-disulfide (21).** Colorless paste (0.305 g, 60%). Three diastereoisomers were found in *ca.* 3 : 4 : 2 intensity ratio. Selected IR (KBr, cm<sup>-1</sup>): 1594(vs), 1499(s), 1462(m), 1408(m), 1296(m), 1259(s), 1180(s), 1114(s), 1025(s), 941(s), 831(m), 803(s), 687(s), 620(s), 538(s). Mass spectrum (CI<sup>+</sup>, m/z), 507 [M+H]<sup>+</sup>. Accurate mass measurement [CI<sup>+</sup>, m/z]: 507.0091 [M+H]<sup>+</sup>, calculated mass for C<sub>19</sub>H<sub>24</sub>O<sub>4</sub>P<sub>2</sub>S<sub>4</sub>H: 507.0105.

**2,9-Bis(4-methoxyphenyl)-1,10-dioxa-3,8-dithia-2,9-diphosphacyclododecane 2,9-disulfide (22).** Colorless paste (0.320 g, 62%). Three diastereoisomers were found in *ca.* 4 : 1 : 5 intensity ratio. Selected IR (KBr, cm<sup>-1</sup>): 1594(vs), 1568(m), 1499(s), 1458(m), 1407(m), 1296(s), 1259(s), 1180(s), 1114(s), 1023(s), 945(s), 830(m), 802(s), 685(s), 619(s), 538(s). Mass spectrum (CI<sup>+</sup>, m/z), 521 [M+H]<sup>+</sup>. Accurate mass measurement [CI<sup>+</sup>, m/z]: 521.0252 [M+H]<sup>+</sup>, calculated mass for C<sub>20</sub>H<sub>26</sub>O<sub>4</sub>P<sub>2</sub>S<sub>4</sub>H: 521.0262.

**3,8-Bis(4-methoxyphenyl)-1,5,6,10-tetrahydrobenzo[e][1,10]dioxo[3,8]dithia[2,9]diphosphacyclododecane 3,8-disulfide (23).** White foam (0.316 g, 56%). Two diastereoisomers were found in *ca.* 2 : 1 intensity ratio. Selected IR (KBr, cm<sup>-1</sup>): 1594(vs), 1500(s), 1455(m), 1408(m), 1297(m), 1259(vs), 1180(m), 1113(vs), 1021(s), 943(s), 830(m), 802(m), 741(m), 687(s), 619(s), 536(s). Mass spectrum (CI<sup>+</sup>, m/z), 569 [M+H]<sup>+</sup>. Accurate mass measurement [CI<sup>+</sup>, m/z]: 569.0269 [M+H]<sup>+</sup>, calculated mass for C<sub>24</sub>H<sub>26</sub>O<sub>4</sub>P<sub>2</sub>S<sub>4</sub>H: 569.0262.

**2,7-Bis(4-methoxyphenyl)-1,8-dioxa-3,6-dithia-2,7-diphosphacycloundecane 2,7-disulfide (24).** Colorless

paste (0.309 g, 61%). Two diastereoisomers were found in *ca.* 1 : 1 intensity ratio. Selected IR (KBr, cm<sup>-1</sup>): 1594(vs), 1567(m), 1499(s), 1459(m), 1407(m), 1296(m), 1259(s), 1179(s), 1114(s), 1025(s), 968(s), 829(m), 802(s), 744(s), 682(s), 617(s), 532(s). Mass spectrum (CI<sup>+</sup>, m/z), 507 [M+H]<sup>+</sup>. Accurate mass measurement [CI<sup>+</sup>, m/z]: 507.0097 [M+H]<sup>+</sup>, calculated mass for C<sub>19</sub>H<sub>24</sub>O<sub>4</sub>P<sub>2</sub>S<sub>4</sub>H: 507.0105.

**4,10-Bis(4-methoxyphenyl)-5,9-dioxa-3,11-dithia-4,10-diphospha-1(1,3)-benzenacyclododecaphane 4,10-disulfide (25).** Golden foam (0.380 g, 65%). Two diastereoisomers were found in *ca.* 1 : 1 intensity ratio. Selected IR (KBr, cm<sup>-1</sup>): 1594(vs), 1500(s), 1460(m), 1408(m), 1296(s), 1259(vs), 1180(s), 1114(vs), 1026(s), 961(s), 830(m), 802(m), 741(m), 688(s), 619(s), 534(s). Mass spectrum (CI<sup>+</sup>, m/z), 583 [M+H]<sup>+</sup>. Accurate mass measurement [CI<sup>+</sup>, m/z]: 583.0413 [M+H]<sup>+</sup>, calculated mass for C<sub>25</sub>H<sub>28</sub>O<sub>4</sub>P<sub>2</sub>S<sub>4</sub>H: 583.0418.

**6,6-Dibutyl-3,9-bis(4-methoxyphenyl)-1,6,7,11-tetrahydro-5H-benzo[e][1,10]dioxo[3,8]dithia[2,9]diphosphacyclotridecane 3,9-disulfide (26).** A white suspension of HOCH<sub>2</sub>C(<sup>n</sup>Bu)<sub>2</sub>CH<sub>2</sub>OH (0.329 g, 1.75 mmol) and NaH (0.16 g, 60%, 4.0 mmol) in THF (60 mL) was heated at 50 °C for 2 h. After cooling to room temperature, **LR** (0.707 g, 1.75 mmol) was added; the mixture was stirred at room temperature for 1 h. Then, 1,2-xylylene dibromide (0.462 g, 1.75 mmol) was added to the above mixture, the mixture was heated again at 50 °C for another 6 h. Upon filtering to remove unreacted solid the filtrate was dried *in vacuo* and the residue was dissolved in dichloromethane (10 mL), after removing the salt by filtration the liquid solution was concentrated to *ca.* 2.0 mL and was loaded onto a silica gel column (50%/50% dichloromethane/hexane as eluent) to give the titled compound **26** as a white solid (0.430 g, 62%). Two diastereoisomers were found in *ca.* 2 : 3 intensity ratio. Selected IR (KBr, cm<sup>-1</sup>): 1592(s), 1571(m), 1501(s), 1459(s), 1298(s), 1259(s), 1179(s), 1114(s), 1029(s), 850(m), 826(m), 801(m), 690(s), 634(m), 622(m), 526(s). Mass spectrum (CI<sup>+</sup>, m/z), 695 [M+H]<sup>+</sup>. Accurate mass measurement [CI<sup>+</sup>, m/z]: 695.1663 [M+H]<sup>+</sup>, calculated mass for C<sub>33</sub>H<sub>44</sub>O<sub>4</sub>P<sub>2</sub>S<sub>4</sub>H: 695.1670.

**7,7-Dibutyl-4,10-bis(4-methoxyphenyl)-5,9-dioxa-3,11-dithia-4,10-diphospha-1(1,3)-benzenacyclododecaphane 4,10-disulfide (27).** A white suspension of HOCH<sub>2</sub>C(<sup>n</sup>Bu)<sub>2</sub>CH<sub>2</sub>OH (0.329 g, 1.75 mmol) and NaH (0.16 g, 60%, 4.0 mmol) in THF (60 mL) was heated at 50 °C for 2 h. After cooling to room temperature, **LR** (0.707 g, 1.75 mmol) was added; the mixture was stirred at room temperature for 1 h. Then, 1,3-xylylene dibromide (0.462 g, 1.75 mmol) was added to the above mixture, the mixture was heated again at 50 °C for another 6 h. Upon filtering to remove unreacted solid the filtrate was dried *in vacuo* and the residue was dissolved in dichloromethane (10 mL), after removing the salt by filtration the liquid solution was concentrated to *ca.* 2.0 mL and was loaded onto a silica gel column (50%/50% dichloromethane/hexane as eluent) to give the titled compound **27** as a colorless paste (0.514 g, 74%).



Two diastereoisomers were found in *ca.* 1 : 1 intensity ratio. Selected IR (KBr,  $\text{cm}^{-1}$ ): 1594(s), 1568(m), 1500(s), 1461(m), 1407(m), 1296(m), 1258(s), 1179(m), 1114(s), 1025(s), 993(s), 830(s), 692(s), 620(s), 534(s). Mass spectrum ( $\text{CI}^+$ ,  $m/z$ ), 695  $[\text{M}+\text{H}]^+$ . Accurate mass measurement [ $\text{CI}^+$ ,  $m/z$ ]: 695.1664  $[\text{M}+\text{H}]^+$ , calculated mass for  $\text{C}_{33}\text{H}_{44}\text{O}_4\text{P}_2\text{S}_4\text{H}$ : 695.1670.

**7,7-Dibutyl-4,10-bis(4-methoxyphenyl)-5,9-dioxo-3,11-dithia-4,10-diphospha-1(1,4)-benzenacyclododecaphane 4,10-disulfide (28).** A white suspension of  $\text{HOCH}_2\text{C}(\text{tBu})_2\text{CH}_2\text{OH}$  (0.329 g, 1.75 mmol) and NaH (0.16 g, 60%, 4.0 mmol) in THF (60 mL) was heated at 50 °C for 2 h. After cooling to room temperature, **LR** (0.707 g, 1.75 mmol) was added; the mixture was stirred at room temperature for 1 h. Then, 1,4-xylylene dibromide (0.462 g, 1.75 mmol) was added to the above mixture, the mixture was heated again at 50 °C for another 6 h. Upon filtering to remove unreacted solid the filtrate was dried *in vacuo* and the residue was dissolved in dichloromethane (10 mL), after removing the salt by filtration the liquid solution was concentrated to *ca.* 2.0 mL and was loaded onto a silica gel column (50%/50% dichloromethane/hexane as eluent) to give the titled compound **28** as a white form (0.460 g, 67%). Two diastereoisomers were found in *ca.* 2 : 1 intensity ratio. Selected IR (KBr,  $\text{cm}^{-1}$ ): 1595(s), 1569(m), 1501(s), 1461(m), 1296(m), 1258(s), 1179(m), 1114(s), 1025(s), 986(s), 830(s), 802(m), 693(s), 620(s), 535(s).  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ), 7.72 (dd,  $J(\text{P},\text{H}) = 13.2$  Hz,  $J(\text{H},\text{H})$ ) Mass spectrum ( $\text{EI}^+$ ,  $m/z$ ), 694  $[\text{M}]^+$ . Accurate mass measurement [ $\text{EI}^+$ ,  $m/z$ ]: 694.1586  $[\text{M}]^+$ , calculated mass for  $\text{C}_{33}\text{H}_{44}\text{O}_4\text{P}_2\text{S}_4$ : 694.1592.

**4,11-Bis(4-methoxyphenyl)-5,10-dioxo-3,12-dithia-4,11-diphospha-1(1,4)-benzenacyclotridecaphan-7-yne 4,11-disulfide (29).** A white suspension of  $\text{HOCH}_2\text{C}\equiv\text{CCH}_2\text{OH}$  (0.086 g, 1.0 mmol) and NaH (0.10 g, 60%, 2.5 mmol) in THF (60 mL) was heated at 50 °C for 2 h. After cooling to room temperature, **LR** (0.404 g, 1.0 mmol) was added; the mixture was stirred at room temperature for 1 h. Then, 1,4-xylylenedibromide (0.264 g, 1.0 mmol) was added to the above mixture, the mixture was heated again at 50 °C for another 6 h. Upon filtering to remove unreacted solid the filtrate was dried *in vacuo* and the residue was dissolved in dichloromethane (10 mL), after removing the salt by filtration the liquid solution was concentrated to *ca.* 2.0 mL and was loaded onto a silica gel column (dichloromethane as eluent) to give the titled compound **29** as white foam (0.455 g, 81%). Two diastereoisomers were found in *ca.* 2 : 1 intensity ratio. Selected IR (KBr,  $\text{cm}^{-1}$ ): 1593(s), 1567(m), 1500(s), 1440(m), 1408(m), 1363(m), 1296(s), 1259(vs), 1180(m), 1113(vs), 1020(s), 972(s), 829(s), 801(s), 692(s), 619(s), 538(s). Mass spectrum ( $\text{CI}^+$ ,  $m/z$ ), 593  $[\text{M}+\text{H}]^+$ . Accurate mass measurement [ $\text{CI}^+$ ,  $m/z$ ]: 593.0256  $[\text{M}+\text{H}]^+$ , calculated mass for  $\text{C}_{26}\text{H}_{26}\text{O}_4\text{P}_2\text{S}_4\text{H}$ : 593.0262.

**6,6-Dibutyl-3,9-diphenyl-1,6,7,11-tetrahydro-5H-benzo[*e*][1,10]dioxo[3,8]diselena[2,9]diphosphacyclotridecine 3,9-diselenide (30).** A white suspension of  $\text{HOCH}_2\text{C}(\text{tBu})_2\text{CH}_2\text{OH}$  (0.188 g, 1.0 mmol) and NaH (0.10 g, 60%, 2.5 mmol) in THF (60 mL) was heated at 50 °C for 2

h. After cooling to room temperature, **WR** (0.54 g, 1.0 mmol) was added; the mixture was stirred at room temperature for 1 h. Then, 1,2-xylylenedibromide (0.264 g, 1.0 mmol) was added to the above mixture, the mixture was heated again at 50 °C for another 6 h. Upon filtering to remove unreacted solid the filtrate was dried *in vacuo* and the residue was dissolved in dichloromethane (10 mL), after removing the salt by filtration the liquid solution was concentrated to *ca.* 2.0 mL and was loaded onto a silica gel column (50%/50% dichloromethane/hexane as eluent) to give the titled compound **30** as pale yellow paste (0.470 g, 57%). Two diastereoisomers were found in *ca.* 3 : 2 intensity ratio. Selected IR (KBr,  $\text{cm}^{-1}$ ): 2361(m), 2339(m), 1494(m), 1456(s), 1377(m), 1219(m), 1186(m), 1017(m), 837(m), 765(s), 737(m), 606(s), 554(m), 533(m), 475(m). Mass spectrum ( $\text{EI}^+$ ,  $m/z$ ), 824  $[\text{M}]^+$ . Accurate mass measurement [ $\text{EI}^+$ ,  $m/z$ ]: 823.9166  $[\text{M}+\text{H}]^+$ , calculated mass for  $\text{C}_{31}\text{H}_{40}\text{O}_2\text{PSe}_4$ : 823.9172.

**7,7-Dibutyl-4,10-diphenyl-5,9-dioxo-3,11-diselena-4,10-diphospha-1(1,3)-benzenacyclododecaphane 4,10-diselenide (31).** A white suspension of  $\text{HOCH}_2\text{C}(\text{tBu})_2\text{CH}_2\text{OH}$  (0.188 g, 1.0 mmol) and NaH (0.10 g, 60%, 2.5 mmol) in THF (60 mL) was heated at 50 °C for 2 h. After cooling to room temperature, **WR** (0.54 g, 1.0 mmol) was added; the mixture was stirred at room temperature for 1 h. Then, 1,3-xylylenedibromide (0.264 g, 1.0 mmol) was added to the above mixture, the mixture was heated again at 50 °C for another 6 h. Upon filtering to remove unreacted solid the filtrate was dried *in vacuo* and the residue was dissolved in dichloromethane (10 mL), after removing the salt by filtration the liquid solution was concentrated to *ca.* 2.0 mL and was loaded onto a silica gel column (50%/50% dichloromethane/hexane as eluent) to give the titled compound **31** as pale green solid (0.401 g, 49%). Two diastereoisomers were found in *ca.* 1 : 1 intensity ratio. Selected IR (KBr,  $\text{cm}^{-1}$ ): 1603(m), 1585(m), 1462(m), 1435(s), 1307(m), 1192(m), 1104(s), 992(vs), 895(m), 828(s), 744(s), 711(m), 688(s), 551(vs), 504(s), 440(m). Mass spectrum ( $\text{EI}^+$ ,  $m/z$ ), 824  $[\text{M}]^+$ . Accurate mass measurement [ $\text{EI}^+$ ,  $m/z$ ]: 823.9168  $[\text{M}]^+$ , calculated mass for  $\text{C}_{31}\text{H}_{40}\text{O}_2\text{PSe}_4$ : 823.9172.

**7,7-Dibutyl-4,10-diphenyl-5,9-dioxo-3,11-diselena-4,10-diphospha-1(1,4)-benzenacyclododecaphane 4,10-diselenide (32).** A white suspension of  $\text{HOCH}_2\text{C}(\text{tBu})_2\text{CH}_2\text{OH}$  (0.188 g, 1.0 mmol) and NaH (0.10 g, 60%, 2.5 mmol) in THF (60 mL) was heated at 50 °C for 2 h. After cooling to room temperature, **WR** (0.54 g, 1.0 mmol) was added; the mixture was stirred at room temperature for 1 h. Then, 1,4-xylylenedibromide (0.264 g, 1.0 mmol) was added to the above mixture, the mixture was heated again at 50 °C for another 6 h. Upon filtering to remove unreacted solid the filtrate was dried *in vacuo* and the residue was dissolved in dichloromethane (10 mL), after removing the salt by filtration the liquid solution was concentrated to *ca.* 2.0 mL and was loaded onto a silica gel column (50%/50% dichloromethane/hexane as eluent) to give the titled compound **32** as pale yellow solid (0.725 g, 88%). Two diastereoisomers were found in *ca.* 2 : 1 intensity ratio.

Selected IR (KBr,  $\text{cm}^{-1}$ ): 1509(m), 1461(m), 1435(s), 1377(m), 1307(m), 1183(s), 1104(s), 1014(vs), 982(vs), 842(vs), 745(s), 712(s), 687(s), 552(vs), 503(s), 440(m). Mass spectrum ( $\text{CI}^+$ ,  $m/z$ ), 825  $[\text{M}+\text{H}]^+$ . Accurate mass measurement [ $\text{CI}^+$ ,  $m/z$ ]: 824.9239  $[\text{M}+\text{H}]^+$ , calculated mass for  $\text{C}_{31}\text{H}_{40}\text{O}_2\text{PSe}_4\text{H}$ : 824.9247.

**11,11-Dibutyl-2,8-diphenyl-1,9-dioxo-3,7-diselena-2,8-diphosphacyclododecane 2,8-diselenide (33).** A white suspension of  $\text{HOCH}_2\text{C}(\text{nBu})_2\text{CH}_2\text{OH}$  (0.188 g, 1.0 mmol) and NaH (0.10 g, 60%, 2.5 mmol) in THF (60 mL) was heated at 50 °C for 2 h. After cooling to room temperature, WR (0.54 g, 1.0 mmol) was added; the mixture was stirred at room temperature for 1 h. Then, 1,3-propanedibromide (0.200 g, 1.0 mmol) was added to the above mixture, the mixture was heated again at 50 °C for another 6 h. Upon filtering to remove unreacted solid the filtrate was dried *in vacuo* and the residue was dissolved in dichloromethane (10 mL), after removing the salt by filtration the liquid solution was concentrated to *ca.* 2.0 mL and was loaded onto a silica gel column (50%/50% dichloromethane/hexane as eluent) to give the titled compound **33** as dark yellow paste (0.400 g, 53%). Two diastereoisomers were found in *ca.* 2 : 5 intensity ratio. Selected IR (KBr,  $\text{cm}^{-1}$ ): 1462(m), 1436(s), 1378(m), 1218(m), 1104(s), 1010(vs), 993(vs), 973(vs), 830(vs), 745(s), 712(s), 688(s), 552(vs), 502(s), 441(m). Mass spectrum ( $\text{CI}^+$ ,  $m/z$ ), 763  $[\text{M}+\text{H}]^+$ . Accurate mass measurement [ $\text{CI}^+$ ,  $m/z$ ]: 762.9089  $[\text{M}+\text{H}]^+$ , calculated mass for  $\text{C}_{26}\text{H}_{38}\text{O}_2\text{PSe}_4\text{H}$ : 762.9089.

**General procedure for synthesis of heterocycles 37 and 38.** A suspension of anhydrous diol (1.0 mmol) and sodium hydride (0.100 g, 60%, 2.5 mmol) in dry THF (60 mL) was heated at 50°C for 1 h leading to a white or pale orange suspension. Upon cooling to ambient temperature the suspension was added WR (0.54 g, 1.0 mmol) and the mixture was allowed to stir at room temperature for 2 h. Then, the appropriate dibromide (1.0 mmol) was added to the mixture and the suspension was continued heating at 50°C for another 6 h giving a grey suspension. Upon filtering to remove unreacted solid the filtrate was dried *in vacuo* and the residue was dissolved in dichloromethane (10 mL), after removing the salt by filtration the liquid solution was concentrated to *ca.* 2.0 mL and was loaded onto a silica gel column (50%/50% dichloromethane/hexane to 100% dichloromethane as eluent) to give the heterocycles **37** and **38**.

**4-Phenyl-3,5-diselena-4-phosphabicyclo[5.4.0]undeca-1(7),8,10-triene-4-selone (37).** An yellow solid (0.310 g, 69%) from the reaction of  $\text{HOCH}(\text{Ph})\text{CH}(\text{Ph})\text{OH}/\text{NaH}$  and WR and  $\alpha,\alpha'$ -dibromo-*o*-xyene. M.p. 195-197 °C. Selected IR (KBr,  $\text{cm}^{-1}$ ): 1434(s), 1179(m), 1090(s), 745(s), 688(m), 535(vs), 488(m). Mass spectrum ( $\text{CI}^+$ ,  $m/z$ ), 451  $[\text{M}+\text{H}]^+$ . Accurate mass measurement [ $\text{CI}^+$ ,  $m/z$ ]: 450.8326  $[\text{M}+\text{H}]^+$ , calculated mass for  $\text{C}_{34}\text{H}_{13}\text{PS}_3\text{H}$ : 450.8337.

**2,4,5-Triphenyl-1,3,2-dioxaphospholane 2-selenide (38).** A greenish yellow paste [0.306 g, 77% yield from the reaction of  $\text{HOCH}(\text{Ph})\text{CH}(\text{Ph})\text{OH}/\text{NaH}/\text{WR}/\alpha,\alpha'$ -dibromo-*o*-xyene; 0.300 g, 75% yield from the reaction of

$\text{HOCH}(\text{Ph})\text{CH}(\text{Ph})\text{OH}/\text{NaH}/\text{WR}/\alpha,\alpha'$ -dibromo-*m*-xyene; 0.320 g, 80% from the reaction of  $\text{HOCH}(\text{Ph})\text{CH}(\text{Ph})\text{OH}/\text{NaH}/\text{WR}/\alpha,\alpha'$ -dibromo-*p*-xyene]. M.p. 186-188°C. Selected IR (KBr,  $\text{cm}^{-1}$ ): 1587(w), 1496(m), 1436(m), 1454(m), 1112(m), 980(s), 856(m), 716(s), 692(s), 637(s), 575(m, P=Se). Mass spectrum [ $\text{CI}^+$ ,  $m/z$ ]: 401  $[\text{M}+\text{H}]^+$ . Accurate mass measurement [ $\text{CI}^+$ ,  $m/z$ ]: 401.0203  $[\text{M}+\text{H}]^+$ , calculated mass for  $\text{C}_{20}\text{H}_{17}\text{O}_2\text{PSeH}$ : 401.0210.

**8,8-Dibutyl-2,5-diphenyl-1,6,3,4,2,5-dioxadiselenadiphosphonane 2,5-diselenide (40).** A white suspension of  $\text{HOCH}_2\text{C}(\text{nBu})_2\text{CH}_2\text{OH}$  (0.329 g, 1.75 mmol) and NaH (0.16 g, 60%, 4.0 mmol) in THF (60 mL) was heated at 50 °C for 2 h. After cooling to room temperature, Woollins' reagent (0.935 g, 1.75 mmol) was added; the mixture was stirred at room temperature for 1 h. Then, *meso*-1,2-dibromide-1,2-phenylethane (0.595 g, 1.75 mmol) was added to the above mixture, the mixture was heated again at 50 °C for another 6 h. Upon filtering to remove unreacted solid the filtrate was dried *in vacuo* and the residue was dissolved in dichloromethane (10 mL), after removing the salt by filtration the liquid solution was concentrated to *ca.* 2.0 mL and was loaded onto a silica gel column (50%/50% dichloromethane/hexane as eluent) to give the titled compound **40** as pale yellow solid (0.968 g, 77%). M.p. 110-112 °C. Selected IR (KBr,  $\text{cm}^{-1}$ ): 2364(w), 2334(w), 1493(m), 1452(m), 1377(m), 1177(m), 1103(s), 1071(m), 1017(s), 985(m), 962(m), 848(m), 762(s), 713(m), 689(s), 555(s), 524(m), 494(s), 466(m), 434(m). Mass spectrum ( $\text{CI}^+$ ,  $m/z$ ), 721  $[\text{M}+\text{H}]^+$ . Accurate mass measurement [ $\text{CI}^+$ ,  $m/z$ ]: 720.8623  $[\text{M}+\text{H}]^+$ , calculated mass for  $\text{C}_{23}\text{H}_{32}\text{O}_2\text{P}_2\text{Se}_4\text{H}$ : 720.8625.

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