JOC The Journal of Organic Chemistry

Article

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# One-Pot Three-Component Condensation Synthesis and Structural Features of Organophosphorus−Sulfur Macrocycles

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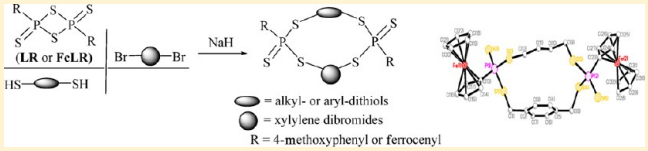
Supporting Information

**ABSTRACT:** A new preparative route was developed to synthesize new phosphorus−sulfur [SP(=S)S moiety]-containing macrocycles via a one-pot and three-component domino reaction of four-membered ring thionation reagents such as 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide (LR, Lawesson's reagent) and 2,4-diferrocenyl-1,3,2,4-diathiadiphosphetane 2,4-disulfide (FcLR, a ferrocene analogue of Lawesson's reagent) and alkyldithiols(aryldithols) and dihaloalkanes in the presence of sodium hydride. Therefore, a series of 12- to 18-membered macrocycles incorporating two phosphorus and six sulfur atoms were synthesized. The synthesis features a novel application of the multicomponent reaction, providing an efficient route to the preparation of the new phosphorus−sulfur-containing macrocycles. Seven representative X-ray structures confirm the formation of these macrocycles and show the presence of a number of the intramolecular C−H···S hydrogen bonding, intermolecular C−H···S, C−H···Cl, and Cl···Cl short contacts and $\pi$-stacking interactions in their 3D network structures.




## INTRODUCTION

Organic macrocycles containing multisulfur linkages are of importance for the study of functions and structures of proteins in chemical biology. They can, in many cases, be used as prodrug molecules due to the organic sulfides displaying a remarkable range of properties in comparison to their oxygen-containing analogues; they can be more nucleophilic, less basic, less polar, and easily oxidized to form sulfoxides and sulfones that provide additional opportunities for structural diversification.[1−10] Phosphorus-containing macrocyclic compounds are also interesting molecules with potential application in supramolecular, coordination, and synthetic organic chemistry.[11−14] Many synthetic methods have been developed such as the preparation of cyclic polysulfides by using either elemental sulfur or other sulfur-transfer reagents. In addition, systematic and selective synthesis of benzene-fused cyclic polysulfides by introduction of bulky substituents on the benzene ring has also been explored.[15−17] However, these methods often give poor yields of the desired products.[18−23] Herein, we report a "one-pot" three-component condensation via a small ring expansion of Lawesson's reagent, a well-known thionation reagent in organic and organometallic syntheses[24,25] or its ferrocene analogue, 2,4-diferrocenyl-1,3,2,4-diathiadiphosphetane 2,4-disulfide (FcLR), by consecutively introducing two organic building blocks to construct a series of phosphorus−sulfur macrocyclic scaffolds incorporating two phosphorus atoms and six sulfur atoms linkages. We aimed at producing a library of phosphorus−sulfur macrocycles in one simple step starting from three simple difunctional building blocks, namely, thionation reagents, dithiols, and dihaloalkanes in the presence of a strong base. To the best of our knowledge, this is the first report of the synthesis and X-ray structure of such organophosphorus−sulfur macrocycles containing the SP($\mu$-S)SC$_n$SP($\mu$-S)S linkage.

## RESULTS AND DISCUSSION

**Synthesis and Characterization.** The two reagents utilized to accomplish a series of one-pot three-component reactions are Lawesson's reagent (LR), which is commercially available, and a ferrocene analogue of Lawesson's reagent, 2,4-diferrocenyl-1,3,2,4-diathiadiphosphetane 2,4-disulfide [FcP($\mu$-S)S]$_2$ (FcLR), for which the preparation, spectroscopic characterization and crystal structure have been reported by our group.[26,27] The one-pot three-component reactions of 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide (LR) with an equimolar amount of dithiol and dibromide in the presence of two equimolar amounts of sodium hydride at room temperature for 24 h led to the corresponding 12- to 16-membered phosphorus−sulfur macrocycles **1**−**10** in 45−67% yields, respectively, as depicted in Scheme 1 and Table 1. In all the cases, insoluble (in water or normal organic solvents such as dichlomomethane, tetrahydrofuran, chloroform, hexane, ethyl ether, acetone, etc.) side products which we were not able to identify, but which we assume are linear polymers, were found resulting in the average yields. The reactions tolerate diverse dithiol substrates such as alkyl-dithiol and aryl-dithiols. Among dibromides, the *o*-xylylene dibromide was found to be preferable for high yields in the current macrocyclization in general, compared to the *m*-xylylene dibromide and *p*-xylylene dibromide; for instance, the combination of the 1,2-benzenedimethanethiol and *o*-xylylene dibromide gave **10** with the

**Received:** March 16, 2016
**Published:** May 2, 2016





DOI: 10.1021/acs.joc.6b00573
J. Org. Chem. 2016, 81, 4210−4225

**Scheme 1. Synthesis of Phosphorus−Sulfur Macrocycles 1−10 (ellipsoid, sphere, and R groups defined in Table 1)**

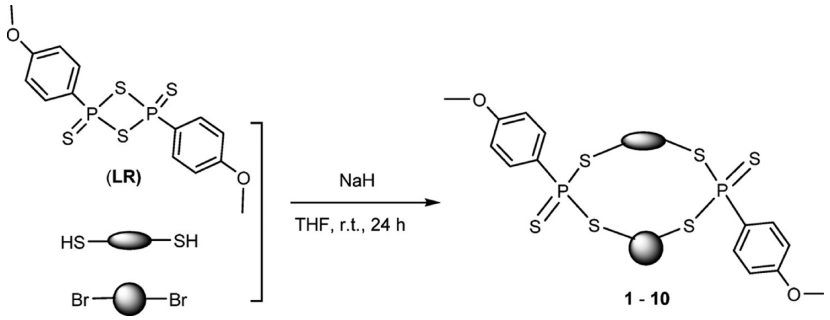



**Table 1. Group Definition, Yields, and $^{31}$P NMR Data of Compounds 1−10**

| Compound | ⬭ | ● | Yield (%) | $^{31}$P NMR (δ, ppm) |
|---|---|---|---|---|
| **1** | $(CH_2)_2$ | 1,2-$CH_2C_6H_4CH_2$ | 45 | 78.9 / 77.8 |
| **2** | $(CH_2)_2$ | 1,3-$CH_2C_6H_4CH_2$ | 65 | 81.3 / 80.9 |
| **3** | $(CH_2)_3$ | 1,2-$CH_2C_6H_4CH_2$ | 59 | 79.5 / 79.1 |
| **4** | $(CH_2)_3$ | 1,3-$CH_2C_6H_4CH_2$ | 55 | 83.1 / 83.0 |
| **5** | $(CH_2)_3$ | 1,4-$CH_2C_6H_4CH_2$ | 58 | 81.5 / 81.2 |
| **6** | $(CH_2)_4$ | 1,2-$CH_2C_6H_4CH_2$ | 45 | 80.4 / 80.2 |
| **7** | $(CH_2)_4$ | 1,3-$CH_2C_6H_4CH_2$ | 56 | 82.1 / 82.0 |
| **8** | $(CH_2)_4$ | 1,4-$CH_2C_6H_4CH_2$ | 49 | 82.7 / 82.6 |
| **9** | 4H-pyrazole-3,5-diyl | 1,4-$CH_2C_6H_4CH_2$ | 46 | 83.3 / 82.8 |
| **10** | 1,2-$CH_2C_6H_4CH_2$ | 1,2-$CH_2C_6H_4CH_2$ | 67 | 77.3 / 77.1 |

**Table 2. Group Definition, Yields, and $^{31}$P NMR Data of Compounds 12−25**

| Compound | ⬭ | ● | Yield (%) | $^{31}$P NMR (δ, ppm) |
|---|---|---|---|---|
| **12** | $(CH_2)_2$ | 1,4-$CH_2C_6H_4CH_2$ | 64 | 81.9 / 81.8 |
| **13** | $(CH_2)_3$ | 1,2-$CH_2C_6H_4CH_2$ | 73 | 79.8 / 79.7 |
| **14** | $(CH_2)_3$ | 1,3-$CH_2C_6H_4CH_2$ | 45 | 82.7 / 80.3 |
| **15** | $(CH_2)_3$ | 1,4-$CH_2C_6H_4CH_2$ | 45 | 80.2 / 79.7 |
| **16** | $(CH_2)_4$ | 1,2-$CH_2C_6H_4CH_2$ | 71 | 79.7 / 79.6 |
| **17** | $(CH_2)_4$ | 1,3-$CH_2C_6H_4CH_2$ | 60 | 81.3 / 81.2 |
| **18** | $(CH_2)_4$ | 1,4-$CH_2C_6H_4CH_2$ | 60 | 81.8 / 81.6 |
| **19** | 4H-pyrazole-3,5-diyl | 1,2-$CH_2C_6H_4CH_2$ | 80 | 95.1 / 95.0 |
| **20** | 4H-pyrazole-3,5-diyl | 1,3-$CH_2C_6H_4CH_2$ | 60 | 83.7 / 82.7 |
| **21** | 4H-pyrazole-3,5-diyl | 1,4-$CH_2C_6H_4CH_2$ | 59 | 80.0 / 79.6 |
| **22** | 1,2-$CH_2C_6H_4CH_2$ | 1,2-$CH_2C_6H_4CH_2$ | 55 | 78.2 / 78.0 |
| **23** | 1,2-$CH_2C_6H_4CH_2$ | 1,3-$CH_2C_6H_4CH_2$ | 64 | 81.6 / 80.2 |
| **24** | 1,2-$CH_2C_6H_4CH_2$ | 1,4-$CH_2C_6H_4CH_2$ | 56 | 81.9 / 81.7 |
| **25** | $(CH_2)_4$ | $(CH_2)_8$ | 46 | 81.6(wide) |

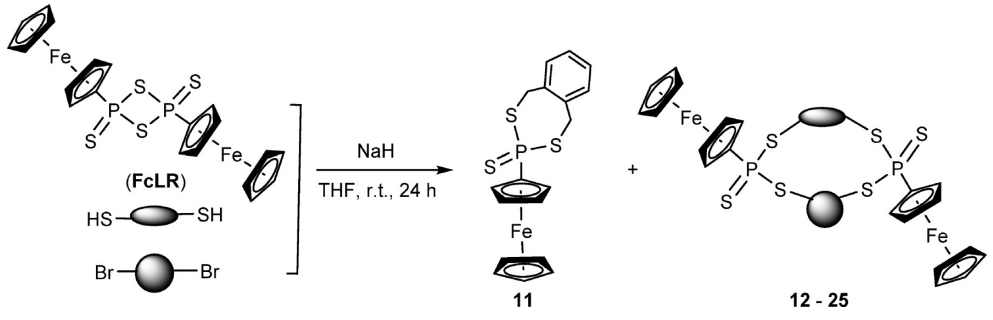
highest yield (67%). It is worth noting that in all cases diastereomeric product was obtained based on the $^{31}$P NMR spectral analyses. The designed, three-component reactions provided a rapid, atom-efficient, and stepwise economic method to construct phosphorus−sulfur macrocycles.

Similarly, the three-component reaction of 2,4-diferrocenyl-1,3,2,4-diathiadiphosphetane 2,4-disulfide $[FcP(\mu\text{-}S)S]_2$ (FcLR) with an equimolar amount of dithiol and dibromide in the presence of two equimolar amounts of sodium hydride at room temperature for 24 h gave rise to the corresponding 12- to 18-membered phosphorus−sulfur macrocycles **12−25** in 40−80% yields as shown in Scheme 2 and Table 2. Surprisingly, a seven-membered heterocycle **11** also formed simultaneously and is isolated in 18% to 24% yields when the *o*-xylylene dibromide was involved as a building block in the reaction. Once again, in all the cases, insoluble (in water or normal organic solvent) byproducts which we were not able to identify were found. The one-pot three-component reactions are satisfactory with dithiol substrates from alkyl-dithiol to aryl-dithios. The results showed that the *o*-xylylene dibromide was preferable to achieve high yields for both macrocycles and heterocycle **11** in the three-component condensation reactions, compared to the *m*-xylylene dibromide and *p*-xylylene dibromide. It is worth noting that in all cases diastereomeric products were obtained.

It is well-known that LR (or FcLR) is believed to be in equilibrium with the monomeric form, which is the true reactive species in solution and can be presented as either of the forms **Ia** and **1b** as shown in Scheme 3.[28,29] Two possible routes (A and B) are assumed to proceed via ring opening and closing reactions for the formation of macrocycles **1−10** and **12−25**. In route A, the reaction of **Ia** or **Ib** proceeds with one molecule of $HSCH_2CH_2SH$/NaH via a nucleophilic opening reaction leading to the disodium dithioate intermediate **II** and is followed by an alkylation of xylylene dibromide, affording the macrocycles by loss of two molecules of NaBr. In route B, **Ia** or **Ib** reacts with one molecule of xylylene dibromide, resulting in P−Br intermediate **III**,[30,31] and the latter cyclizes with $HSCH_2CH_2SH$/NaH, leading to the macrocycles by the loss of two molecules of NaBr and one molecule of $H_2$.

To support and test the proposed mechanisms, route A or B, we chose the preparation of compound **12** as an example. First, we carried out the reaction by following route A: reacting FcLR

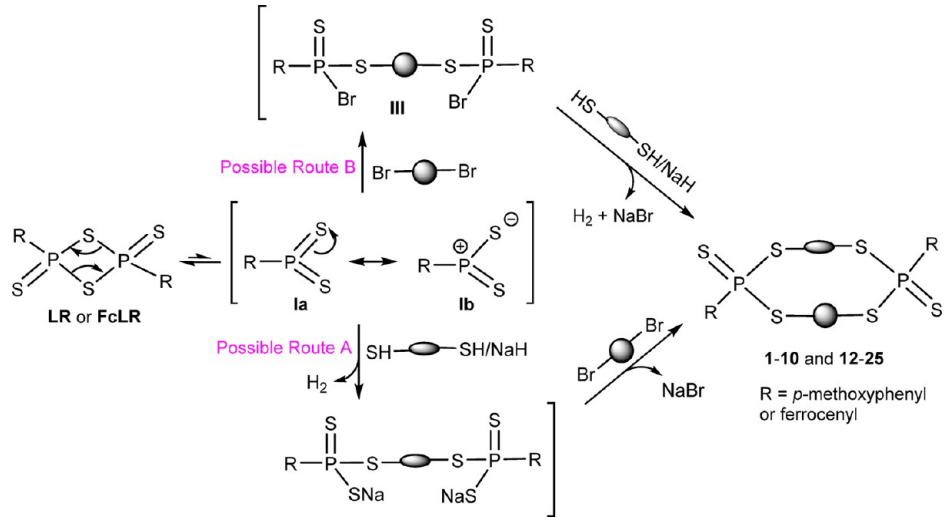
**Scheme 2. Synthesis of Heterocycle 11 and Macrocycles 12−25 (ellipsoid, sphere, and R groups defined in Table 2)**






DOI: 10.1021/acs.joc.6b00573
J. Org. Chem. 2016, 81, 4210−4225

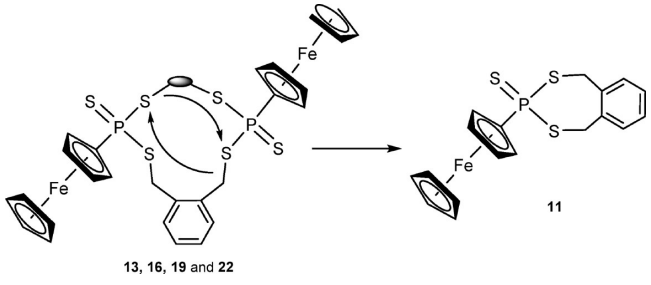
**Scheme 3. Possible Mechanism for the Formation of Macrocycles 1−10 and 12−25**




with 1 equiv of $HSCH_2CH_2SH$/NaH [1:2 molar ratio] at room temperature for 2 h gave the intermediate sodium ethane-1,2-diyl bis(ferrocenylphosphonotrithioate), in which the $^{31}P$ NMR spectrum of the reaction mixture shows one single strong peak $\delta_P$ 70.1 ppm, and the latter was treated in situ with 1 equiv of 1,4-xylylene dibromide at room temperature for 22 h to give the expected macrocycle **12** after purification with a silica gel column. For route B, the reaction of FcLR with 1 equiv of 1,4-xylylene dibromide at room temperature for 10 h led to the assumed P−Br intermediate, in which the $^{31}P$ NMR spectrum of the reaction mixture displays two strong peaks $\delta_P$ 81.8 and 96.1 ppm with equal intensity, indicating the formation of mono- and di-P-Br intermediate. The P−Br intermediate reacted in situ with $HSCH_2CH_2SH$/NaH [1:2 molar ratio] at room temperature for 14 h, resulting in a dark suspension, the $^{31}P$ NMR spectrum of the suspension exhibits one single strong peak $\delta_P$ 69.1 ppm, accompanied by several small peaks, and only small amount of the product (26 mg, $\delta_P$ 59.8 ppm) was obtained after purification with a silica gel column (eluted with 1:4 ethyl acetate/DCM), which was apparently not macrocycle **12** ($\delta_P$ 81.8 and 81.9 ppm), indicating the formation of another unknown product. Thus, the above results suggest that the formation of **1−10** and **12−25** proceeds through route A. In addition, **11** might be the decomposed fragment of the macrocycles **13**, **16**, **19**, and **22** (Scheme 4).

The organophosphorus−sulfur macrocycles **1−25** are soluble in common polar organic solvents and are air- and moisture-stable at ambient temperature for several months without any sign of decomposition. All of the new compounds were characterized by standard analytical and spectroscopic techniques. Two phosphorus atoms in compounds **1− 10** and **12− 25** are potentially stereogenic centers; therefore, stereotypic (*R*,*R*), (*S*,*S*), (*S*,*R*) and (*R*,*S*) stereoisomers are possible. As anticipated, two diastereomers are observed in compounds **1−10** and **12− 24** in their $^{31}P$ NMR spectra though it is not possible to assign them specifically as shown in Tables 1 and 2; however, in **25** there is only one broad signal which might be two signals too close together to identify in its $^{31}P$ NMR spectrum. The $^{1}H$ NMR spectrum reveals disproportionate numerical data for the peak areas (see Supporting Information), confirming that two diastereomers are present. Compounds **1−25** show the anticipated $[M]^+$ or $[M + H]^+$ peak in their mass spectra, satisfactory accurate mass measurements, and appropriate isotopic distributions. The $^{1}H$ NMR and $^{13}C$ NMR spectra of compounds **11−25** display all the characteristic peaks of the ferrocene backbones. The $^{31}P$ NMR spectra of **1−10** and **12−25** exhibit sharp singlets in the range of $\delta$ 77.1 to 95.1 ppm. However, the chemical shifts of compounds **1−10** and **12−25** are clearly different, indicating substantial differences in macrocyclic conformation due to differences in ring current effects. Meanwhile, the $^{31}P$ NMR spectrum of compound **11** also shows a sharp singlet with a lower chemical shift of $\delta$ 50.2 ppm, compared to compounds **1−10** and **12−25**.

**Scheme 4. Possible Mechanism for the Formation of Macrocycle 11**




**Single Crystal Structure Analysis.** Crystals of phosphorus−sulfur macrocycles **5**, **10**, **15**, **18**, **19**, **22**, and **24** suitable for X-ray crystallographic analysis were grown by diffusion of hexane into a dichloromethane solution of the compound. The structures have a single molecule of the compound in the asymmetric unit, except for **10**, which consists of two independent molecules, and compounds **19** and **24**, in which both compounds have a single molecule of the compound and a molecule of dichloromethane. Detailed crystal data and structure refinement for compounds **5**, **10**, **15**, **18**, **19**, **22**, and **24** are collected in Tables 3 and 4. Selected bond lengths and angles are listed in Tables 5 and 6.

The X-ray structures of **5** and **10**, derived from Lawesson's reagent, consist of similar frameworks as shown in Figure 1. The structures confirm that the 15- and 14-membered rings have formed. In the solid state, the structure of **5** adopts a more symmetrical structural pattern than **10**. In both structures, two



DOI: 10.1021/acs.joc.6b00573
J. Org. Chem. 2016, 81, 4210−4225

Table 3. Details of the X-ray Data Collections and Refinements for 5, 10, 15, and 18

| compound | 5 | 10 | 15 | 18 |
|---|---|---|---|---|
| formula | $C_{25}H_{28}O_3P_2S_6$ | $C_{30}H_{30}O_2P_2S_6$ | $C_{31}H_{32}Fe_2P_2S_6$ | $C_{32}H_{34}Fe_2P_2S_6$ |
| $M$ | 614.80 | 676.87 | 770.60 | 784.62 |
| crystal system | orthorhombic | triclinic | triclinic | monoclinic |
| space group | $Cmc2_1$ | $P1$ | $P1$ | $I2/a$ |
| $a$/Å | 34.2(2) | 8.3619(13) | 7.47(4) | 23.798(3) |
| $b$/Å | 11.86(8) | 16.044(3) | 12.42(7) | 7.4405(9) |
| $c$/Å | 6.90(5) | 24.922(4) | 17.85(11) | 37.885(3) |
| $A$ | 90 | 93.773(14) | 101(4) | 90 |
| $B$ | 90 | 99.581(12) | 94(4)(2) | 90.297(8) |
| Γ | 90 | 102.670(12) | 99(4) | 90 |
| $U$/A$^3$ | 2799(32) | 3198.3(9) | 1597(37) | 6708.1(13) |
| $Z$ | 4 | 4 | 2 | 8 |
| $\mu$/cm$^{-1}$ | 6.260 | 5.551 | 14.225 | 13.563 |
| reflections collected | 8618 | 24792 | 11225 | 43287 |
| independent reflections | 2205 | 11179 | 5524 | 6151 |
| $R_{int}$ | 0.0782 | 0.0971 | 0.0930 | 0.1898 |
| $R1$ | 0.0387 | 0.1060 | 0.0799 | 0.0697 |
| $wR2$ [$I > 2\sigma(I)$] | 0.0648 | 0.3003 | 0.1613 | 0.1735 |

Table 4. Details of the X-ray Data Collections and Refinements for 19, 22, and 24

| compound | 19 | 22 | 24 |
|---|---|---|---|
| formula | $C_{31}H_{28}Cl_2Fe_2N_2P_2S_7$ | $C_{36}H_{34}Fe_2P_2S_6$ | $C_{37}H_{36}Cl_2Fe_2P_2S_6$ |
| $M$ | 897.54 | 832.67 | 917.60 |
| crystal system | triclinic | monoclinic | monoclinic |
| space group | $P1$ | $P2_1/n$ | $P2_1/c$ |
| $a$/Å | 8.73(5) | 7.515(6) | 18.848(5) |
| $b$/Å | 13.73(7) | 22.102(13) | 12.694(3) |
| $c$/Å | 15.62(8) | 10.965(8) | 16.584(5) |
| $A$ | 79(3) | 90 | 90 |
| $B$ | 75(3) | 92.82(2) | 95.752(8) |
| Γ | 78(3) | 90 | 90 |
| $U$/A$^3$ | 1750(35) | 1819(2) | 3947.8(19) |
| $Z$ | 2 | 2 | 4 |
| $\mu$/cm$^{-1}$ | 15.178 | 12.556 | 12.954 |
| reflections collected | 12800 | 13577 | 29699 |
| independent reflections | 6102 | 3191 | 6912 |
| $R_{int}$ | 0.0699 | 0.0988 | 0.1115 |
| $R1$ | 0.0507 | 0.0934 | 0.0732 |
| $wR2$ [$I > 2\sigma(I)$] | 0.1129 | 0.1715 | 0.1378 |

swinging *p*-methoxybenzene rings point toward the same side of the cavity, being located above the plane defined by the four inward sulfur atoms. However, the structure of **10** assumes a highly puckered 14-membered ring conformation. Meanwhile, in both **5** and **10**, the exocyclic sulfur atoms on the two phosphorus centers are cis to each other; in addition, all inward atoms (C, S, and P) of the rings are in zigzag position. The angles between the mean plane (defined by four inward sulfur atoms) and the inward phenyl ring(s) are 72.9° in **5**, and 24.1[20.9]° and 23.0[20.3]° in **10**. Two inward phenyl rings in **10** are not parallel, and the dihedral angle is 46.7[41.1]°. The transannular P···P distances of 6.75[6.87] Å in the structure of **10** fall in the ranges that are observed in related P−S-containing macrocycles [4.97−6.97 Å].[32] The transannular P···P length of 8.05 Å in **5** is significantly longer than that observed in **10**, suggesting that the symmetric conformation largely releases the strain of the macrocyclic ring. The geometry around P(1) and P(2) is distorted tetrahedral (S(3)−P(1)−S(1) and S(1)−P(1)−S(2): 113.2(2)° and 106.7(2)° in **5**, and 115.56(16) [115.06(16)]° and 108.84(14)[108.34(16)]° in **10**, being quite similar to those found in the P−Se-containing macrocycles.[32] The P−S single bond lengths in the range of 2.082(4) to 2.110(15) Å and P═S double bonds in the range of 1.934(4) to 1.943(11) Å in the structures of **5** and **10** are typical for the P($\mu$-S)S moiety.[23,34]

The supramolecular assembly in **5** is formed by the intramolecular C−H···S hydrogen bonding [2.680(18) Å with the angle of 125.69°] and intermolecular C−H···S short contacts as shown in Figure 2. The multilayered supramolecular assembly in **10** is supported by the weak intramolecular C−H···S hydrogen bonding and intermolecular C−H···S short contacts and $\pi$-stacking interactions as shown in Figure 3. Interestingly, the intramolecular C−H···S hydrogen bonding is formed by the outward facing S atoms which act as hydrogen bond acceptors toward only hydrogens from the methylene groups attached to the phenyl rings rather than alkyl groups; meanwhile, the outward S atoms act also as hydrogen bond acceptors toward the C−H groups of neighboring phenyl rings



DOI: 10.1021/acs.joc.6b00573
J. Org. Chem. 2016, 81, 4210−4225

**Table 5. Selected Bond Lengths (Å) and Angles (deg) (esds in parentheses) for 5 and 10**

| | compound **5** | compound **10** |
|---|---|---|
| S(1)−P(1) | 2.110(15) | 2.092(3)[2.097(4)] |
| S(2)−P(1) | 2.093(9) | 2.093(3)[2.082(4)] |
| S(3)−P(1) | 1.943(11) | 1.934(4)[1.941(4)] |
| S(4)−P(2) | | 2.087(4)[2.078(4)] |
| S(5)−P(2) | | 2.102(3)[2.100(3)] |
| S(6)−P(2) | | 1.946(4)[1.950(3)] |
| S(1)-C | 1.828(10) | 1.829(9)[1.833(9)] |
| S(2)-C | 1.819(9) | 1.837(12)[1.848(11)] |
| S(4)-C | | 1.835(9)[1.851(10)] |
| S(5)-C | | 1.867(12)[1.860(11)] |
| S(1)−P(1)−S(2) | 106.7(2) | 108.84(14)[108.34(16)] |
| S(1)−P(1)−S(3) | 113.2(2) | 115.56(16)[115.06(16)] |
| S(2)−P(1)−S(3) | 114.6(4) | 106.67(16)[106.83(16)] |
| P(1)−S(1)−C* | 104.13(16) | 97.7(4)[98.6(3)] |
| P(1)−S(2)−C* | 96.4(4) | 101.7(3)[102.4(3)] |
| S(4)−P(2)−S(5) | | 108.15(14)[107.32(14)] |
| S(4)−P(2)−S(6) | | 105.14(17)[107.06(16)] |
| S(5)−P(2)−S(6) | | 116.05(16)[115.78(15)] |
| P(2)−S(5)−C* | | 99.8(3)[96.9(3)] |
| P(2)−S(4)−C* | | 106.2(4)[101.2(4)] |

from another molecule, resulting in a multilayered polymeric architecture in **5**. However, in **10**, the intramolecular C−H···S hydrogen bonds are formed by both the outward S atoms and inward facing S atoms, which act as hydrogen bond acceptors toward hydrogens from the methylene groups attached to the phenyl rings rather than the hydrogens from aryl rings; meanwhile, both outward S atoms and the inward S atoms act as hydrogen bond acceptors toward the C−H groups of a neighboring phenyl rings from another molecule, giving the multilayered polymeric architecture.

The structures of compounds **15**, **18**, **19**, **22**, and **24**, derived from a ferrocene analogue of Lawesson's reagent, 4-diferrocenyl-1,3,2,4-diathiadiphosphetane 2,4-disulfide (FcLR), have similar frameworks as shown in Figure 4. The structures of **15**, **18**, and **24** adopt cradlelike conformations with two ferrocenyl groups lying on the same side and above the cavity; meanwhile, two outward sulfur atoms are located in cis orientations pointing to the opposite side of the two cis ferrocenyl groups and lying below the cavity. However, a boatlike conformation was observed for the structure of **18** with two ferrocenyl groups and two outward sulfur atoms orientating mutually in trans conformation. Interestingly, the structure of **22** gives a highly symmetric conformation in the solid state: the two outward ferrocenyl rings attached to the phosphorus centers and two inward phenyl rings are almost coplanar with the mean plane of the cavity, though the two outward sulfur atoms lie in trans positions. In **15**, the mean plane of four inward sulfur atoms and the inward phenyl ring plane are nearly parallel as measured by a dihedral angle of 4.09°. In **18**, the dihedral angle between the mean plane of four inward sulfur atoms and the inward phenyl ring is 16.24°. In **19**, the inward thiadiazole plane is nearly perpendicular to the plane of the inward phenyl group, as confirmed by a dihedral angle of 79.06°. Surprisingly, the planes of two inward phenyl rings are perfectly parallel to one another and the planes of two Cp rings attached to the phosphorus centers are also nearly parallel to one another in **22**, though the new formed macrocyclic ring is highly skewed. The P···P distances of 6.892 Å in **19** and 6.796 Å in **22** fall in the ranges that are observed in related P−Se macrocycles [4.97−6.97 Å].[32] However, the P···P distances of 7.612 Å in **15**, 8.778 Å in **18** and 8.363 Å in **24** are in contrast to that in **19** and **22** and significantly longer than that observed in P−Se macrocycles [4.97−6.97 Å],[32] indicating the symmetric conformation largely releases the strain of the macrocyclic rings. The geometry around P(1) and P(2) is distorted tetrahedral (S(3)−P(1)−S(1) and S(1)−P(1)−S(2): 104(2)° and 112(2)° in **15**, 105.01(10)° and 108.89(9)° in **18**, 116(2)° and 104.1(12)° in **19**, 115.44(15)° and 106.19(13)° in

**Table 6. Selected Bond Lengths (Å) and Angles (deg) (esds in parentheses) for 15, 18, 19, 22, and 24 (dimensions for second independent molecule in brackets)[a]**

| | **15** | **18** | **19** | **22** | **24** |
|---|---|---|---|---|---|
| S(1)−P(1) | 2.08(7) | 2.087(2) | 2.13(7) | 2.096(4) | 2.086(2) |
| S(2)−P(1) | 2.10(9) | 2.085(2) | 2.12(5) | 2.103(4) | 2.092(2) |
| S(3)−P(1) | 1.95(7) | 1.947(2) | 1.95(3) | 1.949(4) | 1.947(2) |
| S(4)−P(2) | 2.08(6) | 2.100(2) | 2.15(4) | | 2.100(2) |
| S(5)−P(2) | 2.09(8) | 2.087(2) | 2.06(8) | | 2.086(2) |
| S(6)−P(2) | 1.96(8) | 1.940(2) | 1.93(7) | | 1.938(2) |
| S(1)-C* | 1.85(5) | 1.839(6) | 1.75(6) | 1.849(9) | 1.842(6) |
| S(2)-C* | 1.83(6) | 1.820(6) | 1.83(5) | 1.847(8) | 1.843(6) |
| S(4)-C* | 1.84(8) | 1.842(6) | 1.75(6) | | 1.829(6) |
| S(5)-C* | 1.83(3) | 1.822(6) | 1.84(5) | | 1.835(6) |
| S(1)−P(1)−S(2) | 112(2) | 108.89(9) | 104.1(12) | 106.19(13) | 109.53(9) |
| S(1)−P(1)−S(3) | 104(2) | 105.01(10) | 116(2) | 115.44(15) | 115.25(9) |
| S(2)−P(1)−S(3) | 116(3) | 117.53(10) | 114(3) | 108.14(14) | 115.90(9) |
| P(1)−S(1)−C* | 106(3) | 106.5(2) | 98(3) | 102.3(3) | 104.09(19) |
| P(1)−S(2)−C* | 101(4) | 101.0(2) | 108(2) | 107.3(3) | 99.5(3) |
| S(4)−P(2)−S(5) | 109(4) | 110.61(19) | 106.4(16) | | 108.56(10) |
| S(4)−P(2)−S(6) | 106(2) | 116.12(10) | 114(2) | | 116.55(11) |
| S(5)−P(2)−S(6) | 118(3) | 106.46(10) | 118(2) | | 105.37(12) |
| P(2)−S(4)−C* | 105.8(19) | 101.3(2) | 108.6(15) | | 99.5(2) |
| P(2)−S(5)−C* | 102(3) | 102.9(2) | 102.4(18) | | 103.5(2) |

[a]C* might be different numbering in the compound.



DOI: 10.1021/acs.joc.6b00573
J. Org. Chem. 2016, 81, 4210−4225

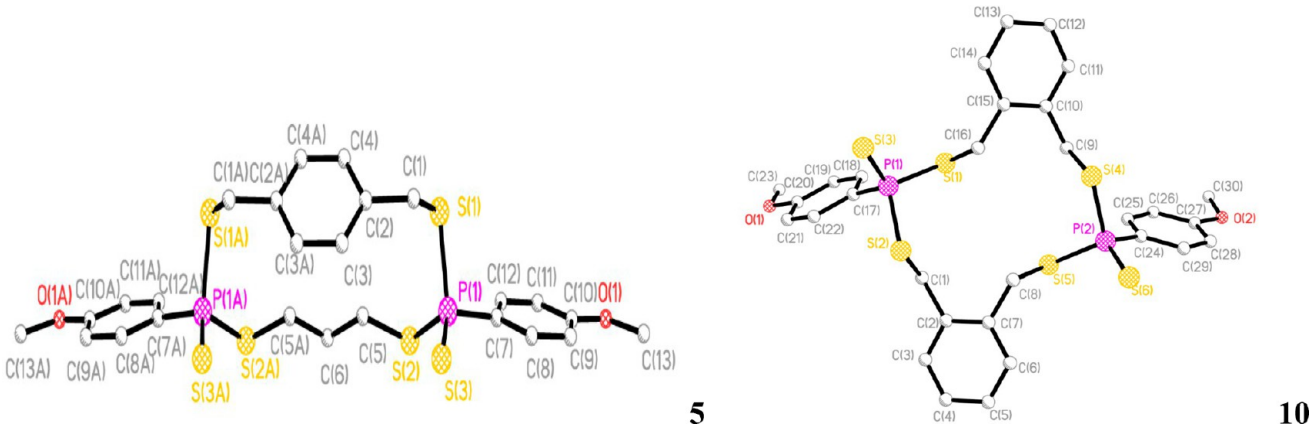



**Figure 1.** Single crystal X-ray structures of compounds **5** and **10**.

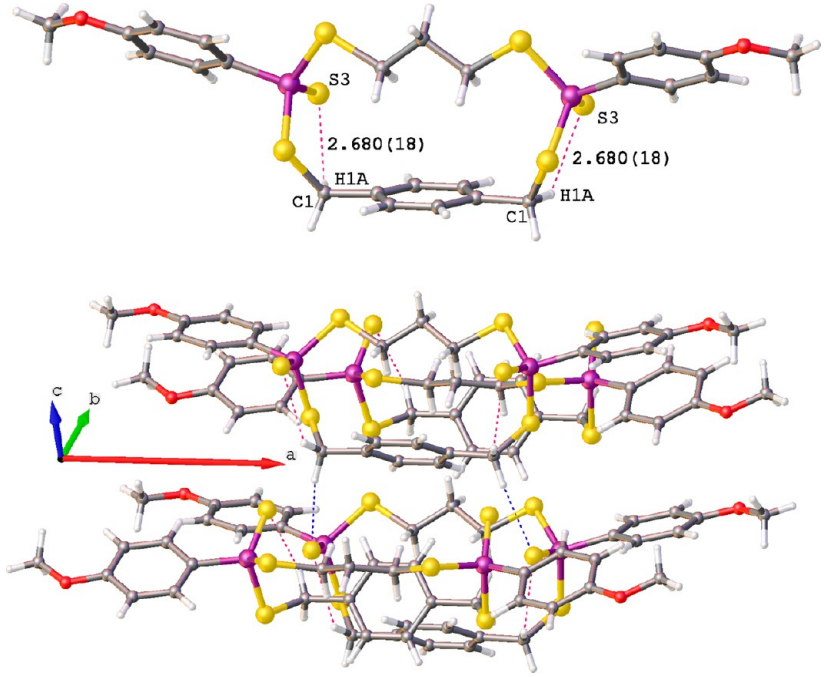



**Figure 2.** Upper diagram shows the intramolecular C(1)−H(1A)···S(3) hydrogen bond [2.680(18) Å with the angle of 125.69°] in **5**. Lower diagram shows the intramolecular C−H···S hydrogen bonds and intermolecular C−H···S short contacts in the supramolecular assembly of **5**.

**22**, and 115.25(9)° and 109.53(9)° in **24**, being quite similar to those found in the P−Se-containing macrocycles.[32] The P−S−C bond angles range from 98(3)° to 108.6(15)°, reflecting a significant degree of ring strain in these macrocyclic compounds. The P−S single bond lengths in the range of 2.06(8) to 2.15(4) Å and P═S double bond lengths in the range of 1.93(7) to 1.96(8) Å in **15**, **18**, **19**, **22**, and **24** are the typical for the P($\mu$-S)S moiety.[33,34]

In the supramolecular structures of **15**, **18**, **19**, **22**, and **24**, a number of the intramolecular C−H···S hydrogen bonds, intermolecular C−H···S, C−H···O, C−H···N, C−H···Cl, and Cl···Cl short interactions, and $\pi$-stacking interactions are observed (Figures 5−9). The structures of **15** and **18** have highly similar packing motifs with the intramolecular C−H···S hydrogen bonding, intermolecular C−H···S short contacts, and $\pi$-stacking interactions to stabilize the three-dimensional frameworks. Both inward phenyl group and methylene groups in **15** and **18** act as different hydrogen-bond donors in the intramolecular hydrogen bonding, where the acceptors are the outward and inward sulfur atoms from the same molecule; in addition to the intermolecular close contacts, not only the inward phenyl group and methylene groups acting as hydrogen-bond donors and the outward and inward sulfur atoms as acceptors but also the ferrocenyl rings from the neighboring molecules act as hydrogen-bond donors. However, the packing structure of **19** reveals a different three-dimensional network, compared to the supramolecular frameworks of **15** and **18**, because intermolecular C−H···Cl short contacts are observed, where the dichloromethane solvent molecules act as double solvent bridges between two layers.[35] The H···Cl distance (2.856 Å) is marginally shorter than that reported previously (2.90 Å).[36] Additional intermolecular Cl···Cl short contacts [3.244 Å, shorter than the van der Waal radii sum (3.6 Å)] are found between two solvent molecules to stabilize the packing in the lattice.[37] Though **21** and **24** have highly similar gross molecular structures with inward facing phenyl groups, the presence of cocrystallized dichloromethane solvent has a significant effect in the supramolecular structure of **24**,



DOI: 10.1021/acs.joc.6b00573
J. Org. Chem. 2016, 81, 4210−4225

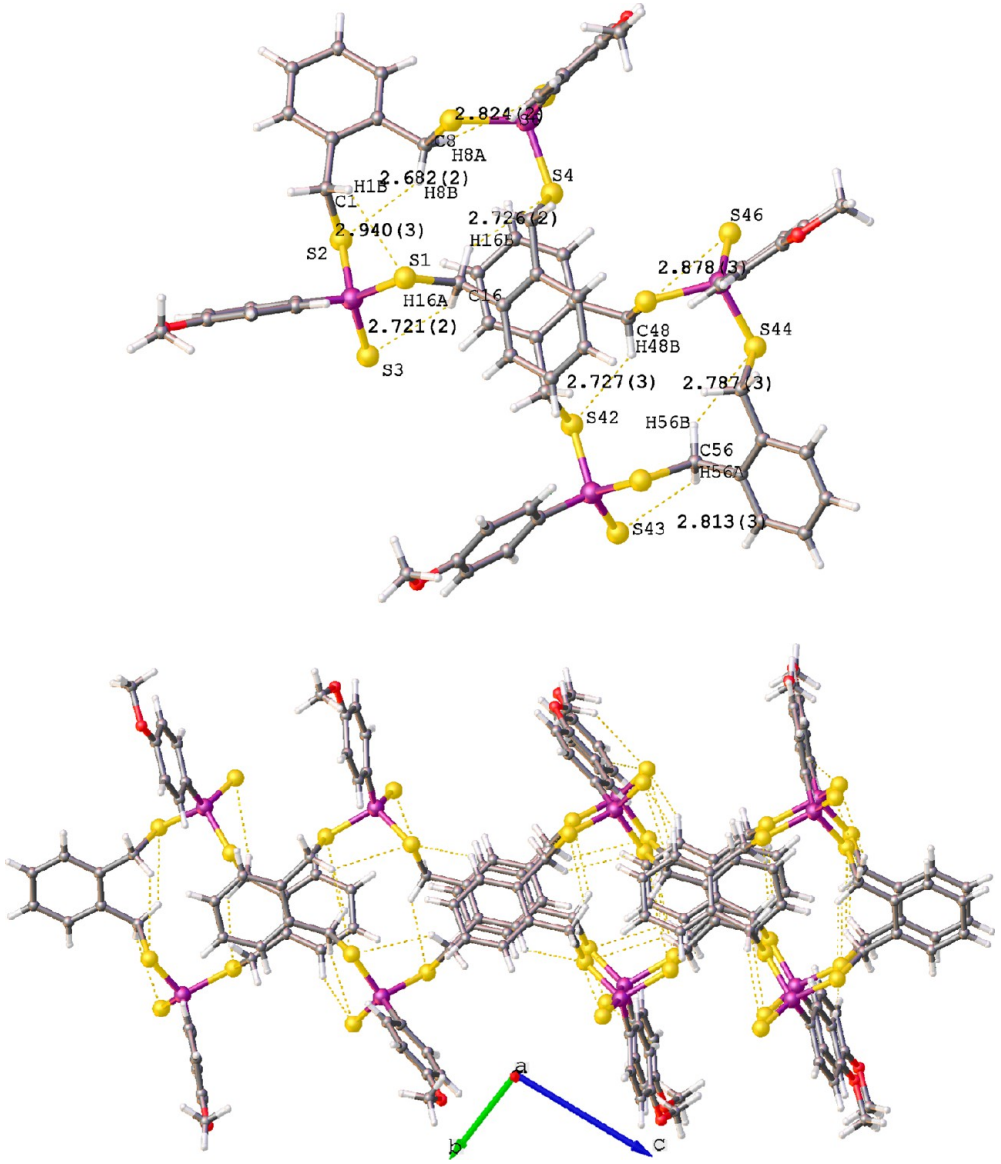



**Figure 3.** Upper diagram shows the intramolecular hydrogen bonds between outward S(2) and H(8B) {2.940(3)[2.727(3)] Å with the C(8)−H(8B)···S(2) angle of 134.26[133.35]°}, between outward S(3) and H(16A) {2.721(2)[2.813(3)] Å with the C(16)−H(16A)···S(3) angle of 131.30[127.63]°] Å}, between inward S(4) and H(16B) {2.726(2)[2.787(3)] Å with the C(16)−H(16B)···S(4) angle of 132.71[133.05]°} and between inward S(6) and H(8A) {2.824(2)[2.878(3)] Å with the C(8)−H(8A)···S(6) angle of 129.20[127.20]°} in **10**. Lower diagram shows the intramolecular C−H···S hydrogen bonds and intermolecular C−H···S short contacts and $\pi$-stacking interactions in the supramolecular assembly of **10**.

compared to **22** where all sulfur atoms act as hydrogen-bond acceptors and both the methylene groups and phenyl groups act as hydrogen-bond donors. However, in **24**, two outward sulfur atoms act as hydrogen-bond acceptors and only half of the inward sulfur atoms act as hydrogen-bond acceptors. Once again, intermolecular C−H···Cl short interactions, where the dichloromethane solvent molecules act as double solvent bridges between two layers, are observed to stabilize the three-dimensional framework in **24**; however, no intermolecular Cl···Cl short contacts are found.

In summary, we have successfully developed a highly efficient route for the synthesis of a series of structurally novel 12- to 18-membered organophosphorus−sulfur macrocycles via a one-pot three-component condensation of four-membered ring thionation reagent, 2,4-bis(4-methoxyphenyl)-1,3,2,4-dithiadiphosphetane 2,4-disulfide (LR, Lawesson's reagent) or 2,4-diferrocenyl-1,3,2,4-diathiadiphosphetane 2,4-disulfide (FcLR, a ferrocene analogue of Lawesson's reagent), alkenyl-dithiols or aryl-dithiols, and dihaloalkanes in the presence of sodium hydride. Seven representative X-ray structures are discussed to confirm the formation of these macrocycles. The resulting data reveal the number of intramolecular C−H···S hydrogen bonds, intermolecular C−H···S, C−H···Cl and Cl···Cl short contacts, and $\pi$-stacking interactions observed leading to the multilayered supramolecular structures. The reported results enhance the application of the multicomponent reaction further, providing an efficient and environmentally benign route to the preparation of the unusual up to 18-membered phosphorus−sulfur macrocycles. The coordination chemistry of these multiple sufur organophosphorus macrocycles will be investigated in due course.



DOI: 10.1021/acs.joc.6b00573
J. Org. Chem. 2016, 81, 4210−4225

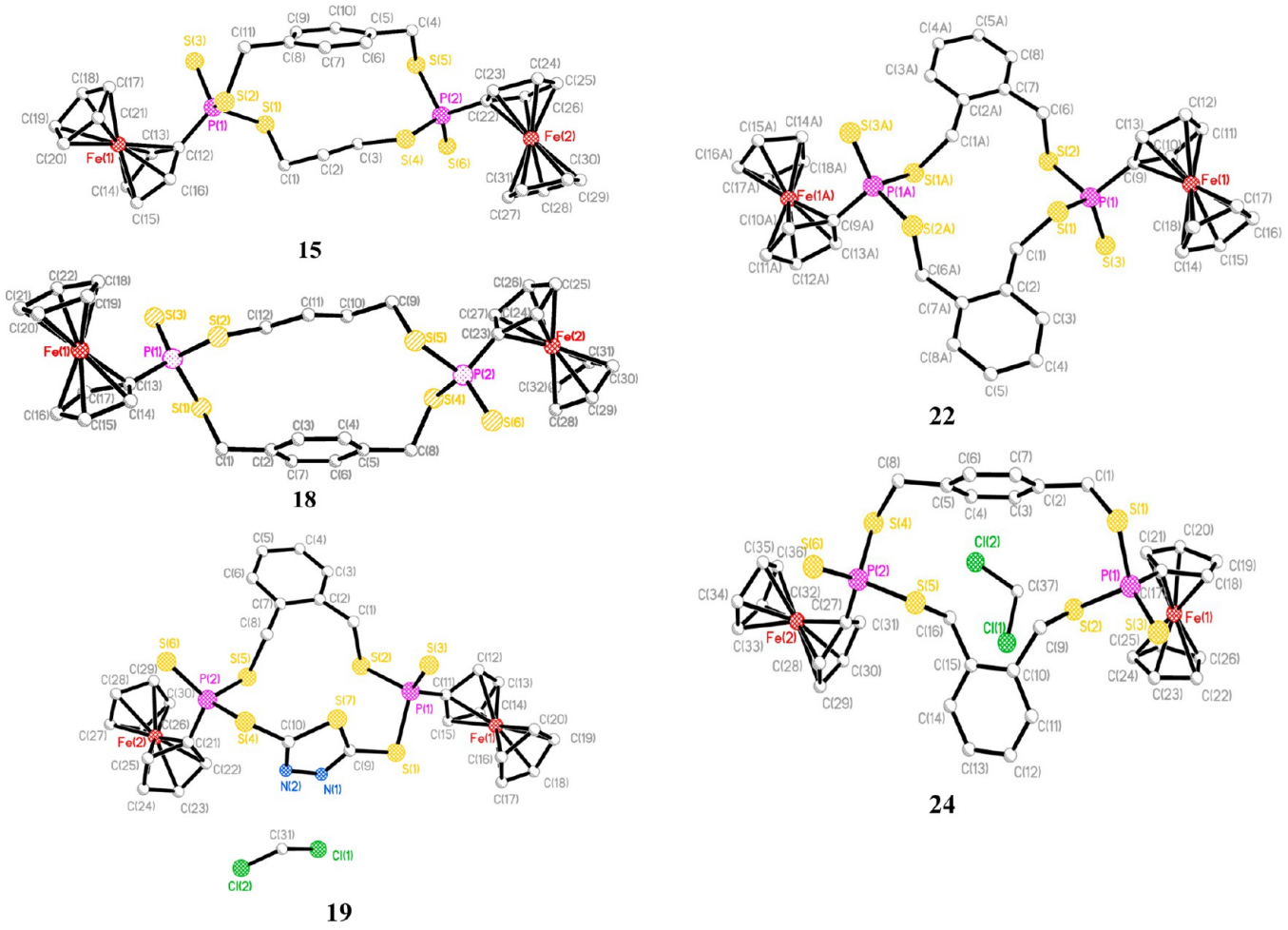



**Figure 4.** Single crystal X-ray structures of compounds **15**, **18**, **19**, **22**, and **24**.

## EXPERIMENTAL SECTION

Unless otherwise stated, all reactions were carried out under an oxygen-free nitrogen atmosphere using predried solvents and standard Schlenk techniques. Subsequent chromatographic and workup procedures were performed in air. All commercially available reagents including alkyldithiols and aryldithiols were used as supplied without further purification unless stated otherwise. $^{1}$H (400.1 MHz), $^{13}$C (100.6 MHz), and $^{31}$P-{$^{1}$H} (162.0 MHz) NMR spectra were recorded at 25 °C. IR spectra were recorded as KBr pellets in the range of 4000−250 cm$^{-1}$. Mass spectrometry ($m/z$, HRMS) was performed using either atmospheric pressure chemical ionization (APCI) or electron ionization (EI) using a TOM mass analyzer. X-ray crystal data for compounds **5**, **10**, **15**, **18**, **19**, **22**, and **24** were collected using $\omega$ steps, accumulating area detector images spanning at least one 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 semiempirical methods. Structures were solved by direct methods and refined by full-matrix least-squares against $F^2$ by using the program SHELXTL.[38] 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 or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax (+44) 1223−336−033; e-mail: deposit@ccdc.cam.ac.uk. CCDC nos. 1468813−1468819.

**General Procedure for Preparation of Macrocycles 1−10.** A suspension of alkyldithiol or aryldithiol (2.0 mmol), sodium hydride (0.16 g, 60% suspension in oil, 4.0 mmol), LR (0.808 g, 2.0 mmol), and xylylene dibromide (0.528 g, 2.0 mmol) in dry THF (60 mL) was stirred at room temperature for 24 h, giving a yellowish white or off-white suspension. Upon filtration to remove unreacted solid, the filtrate was dried in vacuo and the residue was dissolved in dichloromethane (10 mL). After removal of the salt by filtration, the liquid solution was concentrated to ca. 2 mL and was loaded onto a silica gel column (dichloromethane as eluent) to give compounds **1**−**10**.

*3,8-Bis(4-methoxyphenyl)-1,5,6,10-tetrahydrobenzo[j][1,3,6,8]-tetrathia[2,7]diphosphacyclododecine 3,8-Disulfide (1).* Colorless sticky paste [0.58 g, 45% based on LR (2.13 mmol)]. Two diastereoisomers were found in ca. 1:1 intensity ratio. Selected IR (KBr, cm$^{-1}$): 1591(s), 1564(m), 1494(s), 1455(m), 1438(m), 1406(m), 1294(m), 1294(s), 1178(s), 1098(s), 1022(s), 828(s), 799(m), 765(m), 686(vs), 618(s), 535(s), 500(s), 451(m). $^{1}$H NMR ($CD_2Cl_2$, $\delta$), 8.09−8.00 (m, 4H), 7.86−7.80 (m, 8H), 7.68−7.60 (m, 8H), 7.57−7.47 (m, 4H), 4.37−4.21 (m, 8H), 4.06 (s, 6H), 3.98 (s, 6H), 3.57−2.62 (m, 8H) ppm. $^{13}$C NMR ($CD_2Cl_2$, $\delta$), 164.1, 164.0, 135.7, 135.6, 134.4, 133.8, 133.6, 133.0, 132.8, 131.0, 130.5, 129.5, 115.3, 115.2, 58.5, 58.4, 38.3, 37.9, 35.8, 34.7 ppm. $^{31}$P NMR ($CD_2Cl_2$, $\delta$), 78.9 and 77.8 ppm. Mass spectrum (EI$^+$, $m/z$), 600 [M]$^+$. Accurate mass measurement [EI$^+$, $m/z$]: 599.9728 [M]$^+$, calculated mass for $C_{24}H_{26}O_2P_2S_6$: 599.9727.

*4,9-Bis(4-methoxyphenyl)-3,5,8,10-tetrathia-4,9-diphospha-1-(1,3)-benzenacycloundecaphane 4,9-Disulfide (2).* White paste [1.17 g, 65% based on LR (3.0 mmol)]. Two diastereoisomers were found in ca. 3:2 intensity ratio. Selected IR (KBr, cm$^{-1}$): 1591(s), 1565(m), 1495(s), 1459(m), 1405(m), 1293(m), 1257(s), 1178(s), 1098(s), 1023(m), 828(m), 799(m), 687(s), 618(m), 534(s), 502(m). $^{1}$H NMR ($CD_2Cl_2$, $\delta$), 7.90−7.80 (m, 8H), 7.20−6.91 (m, 16H), 4.38−4.28 (m, 4H), 4.16−3.90 (m, 4H), 3.77 (s, 6H), 3.76 (s, 6H), 3.11−3.04 (m, 4H), 3.00−2.63 (m, 4H) ppm. $^{13}$C NMR ($CD_2Cl_2$, $\delta$), 163.2,



DOI: 10.1021/acs.joc.6b00573
J. Org. Chem. 2016, 81, 4210−4225

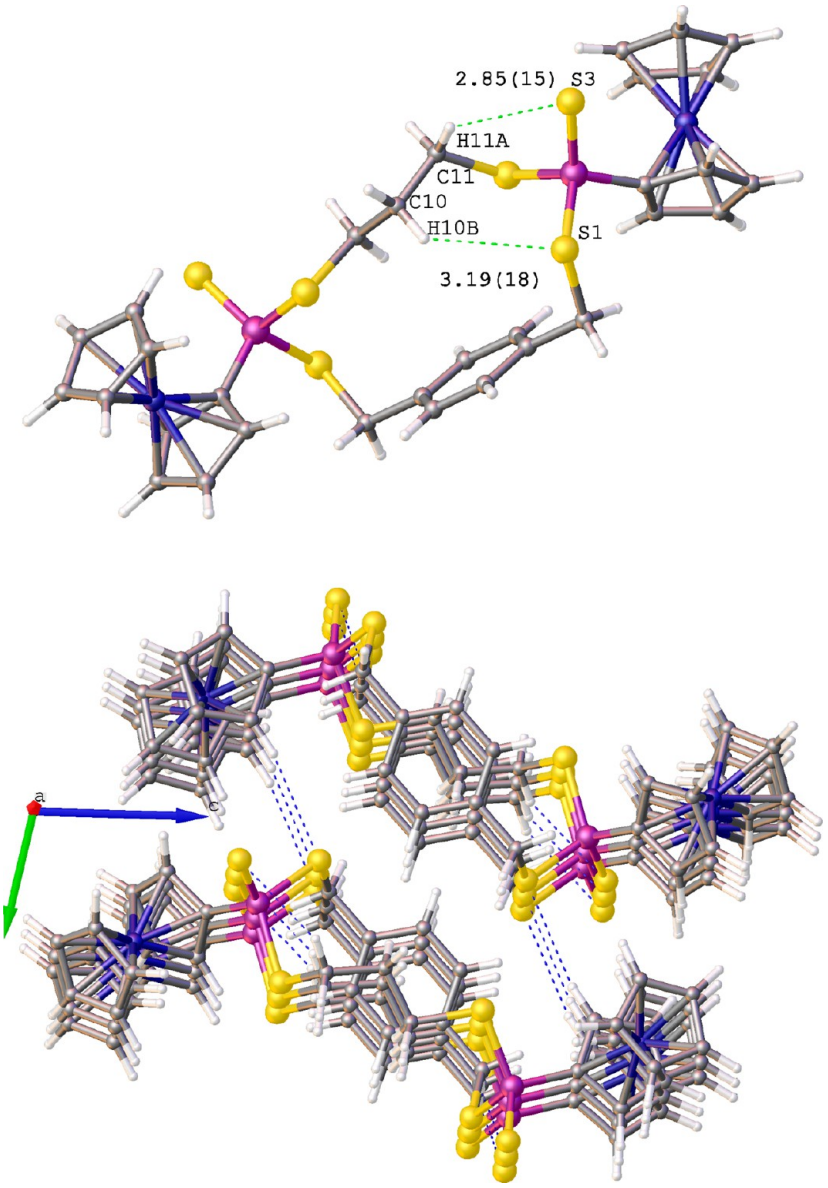



**Figure 5.** The upper diagram shows the intramolecular C(10)−H(10B)···S(1) and C(11)−H(11A)···S(3) hydrogen bonds [3.19(18) and 2.85(15) Å with the angles of 137.25° and 129.98°] in **15**. The lower diagram shows the intramolecular C−H···S hydrogen bonds and intermolecular C−H···S short contacts and $\pi$-stacking interactions in the supramolecular assembly of **15**.

163.1, 139.0, 138.4, 136.9, 132.9, 132.8, 132.4, 132.2, 131.3, 130.8, 128.9, 128.6, 128.4, 114.4, 114.1, 55.6, 38.6, 37.6, 33.2, 33.1 ppm. $^{31}$P NMR ($CD_2Cl_2$, $\delta$), 81.3 and 80.9 ppm. Mass spectrum (EI$^+$, $m/z$), 600 [M]$^+$. Accurate mass measurement [EI$^+$, $m/z$]: 599.9723 [M]$^+$, calculated mass for $C_{24}H_{26}O_2P_2S_6$: 599.9727.

*4,9-Bis(4-methoxyphenyl)-3,5,8,10-tetrathia-4,9-diphospha-1-(1,4)-benzenacycloundecaphane 4,9-Disulfide (**3**).* White solid [0.926 g, 58% based on LR (2.66 mmol)]. Two diastereoisomers were found in ca. 1:2 intensity ratio. Selected IR (KBr, cm$^{-1}$): 1591(s), 1564(m), 1495(s), 1459(m), 1406(m), 1293(m), 1256(s), 1178(s), 1098(s), 1023(s), 828(m), 799(m), 687(s), 618(m), 533(s), 501(m). $^1$H NMR ($CD_2Cl_2$, $\delta$), 7.89−7.86 (m, 8H), 7.47−6.93 (m, 20H), 4.44−4.33 (m, 4H), 4.22−4.02 (m, 4H), 3.84 (s, 6H), 3.82 (s, 6H), 3.72−3.65 (m, 4H), 3.18−2.29 (m, 4H) ppm. $^{13}$C NMR ($CD_2Cl_2$, $\delta$), 163.2, 137.2, 135.9, 133.0, 132.8, 131.9, 131.7, 130.7, 130.2, 129.9, 129.5, 129.3, 128.3, 114.3, 114.0, 55.7, 42.8, 37.7, 34.1, 25.3 ppm. $^{31}$P NMR ($CD_2Cl_2$, $\delta$), 79.9 and 79.7 ppm. Mass spectrum (EI$^+$, $m/z$), 600 [M]$^+$. Accurate mass measurement [EI$^+$, $m/z$]: 599.9729 [M]$^+$, calculated mass for $C_{24}H_{26}O_2P_2S_6$: 599.9727.

*3,9-Bis(4-methoxyphenyl)-1,6,7,11-tetrahydro-5H-benzo[k]-[1,3,7,9]tetrathia[2,8]-diphosphacyclotridecine 3,9-Disulfide (**4**).* Off-white foam [1.313 g, 73% based on LR (2.45 mmol)]. Two diastereoisomers were found in ca. 1:3 intensity ratio. Selected IR (KBr, cm$^{-1}$): 1591(s), 1564(m), 1494(s), 1456(m), 1438(m), 1405(m), 1293(m), 1256(s), 1178(s), 1098(s), 1022(s), 828(s), 799(m), 766(m), 687(s), 618(m), 535(s), 501(m). $^1$H NMR ($CD_2Cl_2$, $\delta$), 8.10−8.02 (m, 8H), 7.35−7.28 (m, 8H), 7.12−6.97 (m, 8H), 4.37−4.29 (m, 8H), 3.92 (s, 6H), 3.91 (s, 6H), 3.88−3.03 (m, 8H), 2.52−2.38 (m, 2H), 2.29−2.08 (m, 2H) ppm. $^{13}$C NMR ($CD_2Cl_2$, $\delta$), 163.3, 163.1, 134.2, 134.1, 132.9, 132.7, 132.3, 132.1, 131.6, 131.3, 128.8, 128.7, 114.5, 114.3, 55.6, 55.5, 37.1, 36.2, 35.6, 33.0, 32.7, 29.8 ppm. Mass spectrum (EI$^+$, $m/z$), 614 [M]$^+$. Accurate mass measurement [EI$^+$, $m/z$]: 613.9884 [M]$^+$, calculated mass for $C_{25}H_{28}O_2P_2S_6$: 613.9883.

*4,10-Bis(4-methoxyphenyl)-3,5,9,11-tetrathia-4,10-diphospha-1-(1,4)-benzenacyclododecaphane 4,10-Disulfide (**5**).* White foam [0.55 g, 45% based on LR (2.0 mmol)]. Two diastereoisomers were found in ca. 1:2 intensity ratio. Selected IR (KBr, cm$^{-1}$): 1591(s), 1564(m), 1495(s), 1404(m), 1293(s), 1256(s), 1178(s), 1098(s),



DOI: 10.1021/acs.joc.6b00573
J. Org. Chem. 2016, 81, 4210−4225

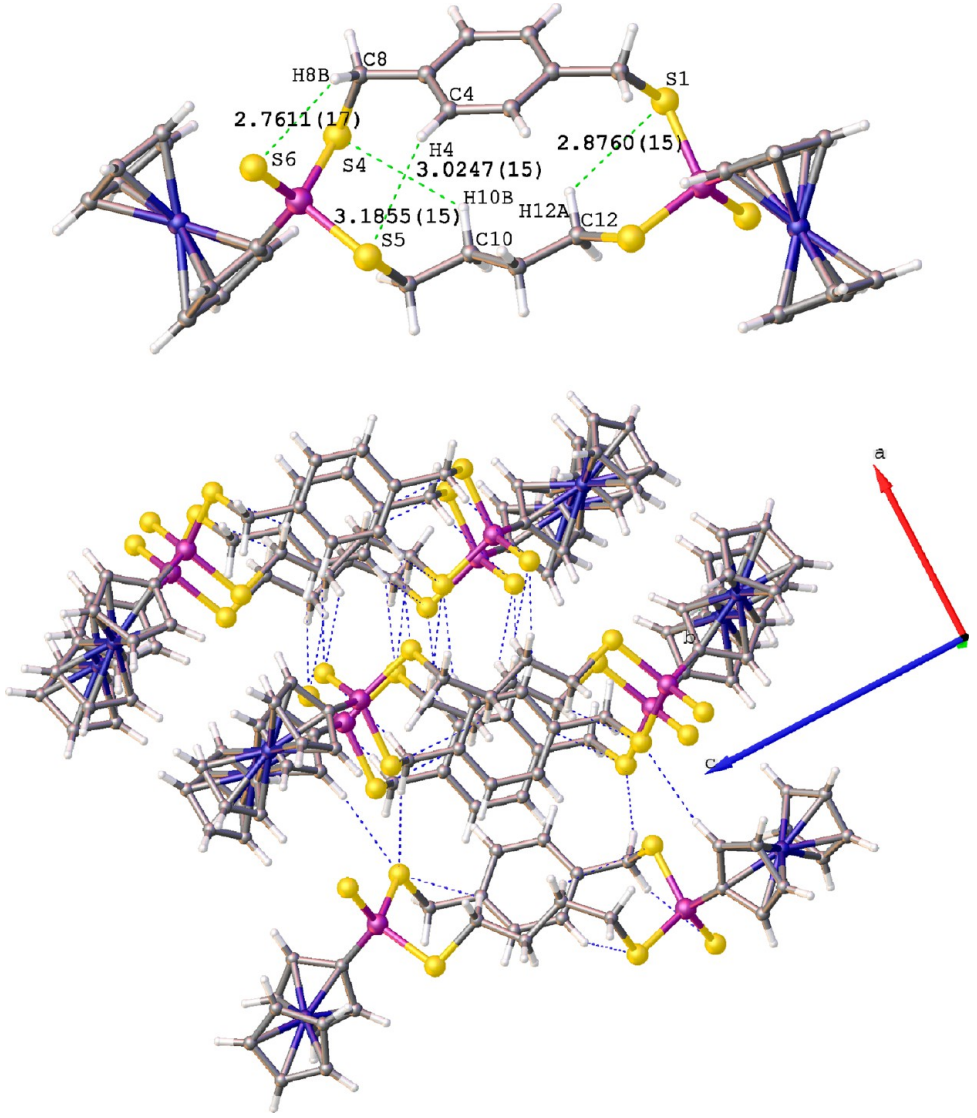



**Figure 6.** The upper diagram shows the intramolecular C(12)−H(12A)···S(1), C(10)−H(10B)···S(1), C(4)−H(4)···S(5) and C(8)−H(8B)···S(6) hydrogen bonds [2.8760(15), 3.247(15), 3.18855(15) and 2.7611(17) with the angles of 120.98°, 128.13°, 128.13°, and 131.58°] in **18**. The lower diagram shows the intramolecular hydrogen bonds and intermolecular C−H···S short contacts and $\pi$-stacking interactions in the supramolecular assembly of **18**.

1022(s), 827(s), 799(s), 684(s), 617(s), 535(s), 501(m). $^{1}$H NMR ($CD_2Cl_2$, $\delta$), 7.88−7.81 (m, 8H), 7.39−7.36 (m, 8H), 6.96−6.91 (m, 8H), 4.40−4.25 (m, 4H), 4.11−3.94 (m, 4H), 3.78 (s, 6H), 3.77 (s, 6H), 2.40−2.25 (m, 8H), 1.78−1.71 (m, 2H), 1.65−1.54 (m, 2H) ppm. $^{13}$C NMR ($CD_2Cl_2$, $\delta$), 163.4, 163.3, 138.2, 138.0, 133.1, 132.6, 132.5, 132.4, 132.3, 130.3, 130.0, 129.8, 128.1, 126.9, 114.5, 114.3, 56.0, 38.0, 37.6, 33.1, 32.8, 28.4, 28.0 ppm. $^{31}$P NMR ($CD_2Cl_2$, $\delta$), 80.2 and 79.7 ppm. Mass spectrum ($EI^+$, $m/z$), 614 $[M]^+$. Accurate mass measurement [$EI^+$, $m/z$]: 613.9880 $[M]^+$, calculated mass for $C_{25}H_{28}O_2P_2S_6$: 613.9883.

*3,10-Bis(4-methoxyphenyl)-1,5,6,7,8,12-hexahydrobenzo[e]-[1,3,8,10]tetrathia[2,9]-diphosphacyclotetradecine 3,10-Disulfide* (***6***). White foam [0.645 g, 71% based on LR (1.44 mmol)]. Two diastereoisomers were found in ca. 2:3 intensity ratio. Selected IR (KBr, $cm^{-1}$): 1591(s), 1565(m), 1495(s), 1439(m), 1405(m), 1293(m), 1257(s), 1178(s), 1098(s), 1023(m), 828(m), 799(m), 686(s), 618(s), 536(s), 501(m), 446(m). $^{1}$H NMR ($CD_2Cl_2$, $\delta$), 7.92 (d, $J$(H,H) = 8.5 Hz, 4H), 7.89 (d, $J$(H,H) = 8.5 Hz, 4H), 7.20−7.10 (m, 8H), 6.96−6.91 (m, 8H), 4.26−4.03 (m, 8H), 3.76 (s, 6H), 3.72 (s, 6H), 3.12−2.87 (m, 8H), 1.73−1.57 (m, 4H), 1.33−1.17 (m, 4H) ppm. $^{13}$C NMR ($CD_2Cl_2$, $\delta$), 163.6, 163.5, 135.5, 134.9, 133.2 (d, $J$(P,C) = 13.6 Hz), 132.7 (d, $J$(P,C) = 13.6 Hz), 131.6, 131.4, 128.6, 128.5, 127.5, 127.3, 114.9, 114.7, 56.1, 36.4, 36.0, 34.0, 33.4, 28.3, 28.1 ppm. $^{31}$P NMR ($CD_2Cl_2$, $\delta$), 79.7 and 79.6 ppm. Mass spectrum ($CI^+$, $m/z$), 629 $[M + H]^+$. Accurate mass measurement [$CI^+$, $m/z$]: 629.0117 $[M + H]^+$, calculated mass for $C_{26}H_{30}O_2P_2S_6H$: 629.0118.

*4,11-Bis(4-methoxyphenyl)-3,5,10,12-tetrathia-4,11-diphospha-1(1,3)-benzenacyclotridecaphane 4,11-Disulfide* (***7***). White foam [0.655 g, 60% based on LR (1.75 mmol)]. Two diastereoisomers were found in ca. 1:2 intensity ratio. Selected IR (KBr, $cm^{-1}$): 1591(s), 1565(m), 1495(s), 1439(m), 1405(m), 1293(s), 1265(s), 1177(s), 1098(s), 1023(m), 827(s), 799(s), 685(s), 618(s), 534(s), 501(m). $^{1}$H NMR ($CD_2Cl_2$, $\delta$), 7.92−7.86 (m, 8H), 7.15−6.90 (m, 16H), 4.25−4.14 (m, 4H), 3.96−3.90 (m, 4H), 3.77 (s, 6H), 3.76 (s, 6H), 3.75−3.72 (m, 4H), 2.96−2.69 (m, 4H), 1.78−1.60 (m, 8H) ppm. $^{13}$C NMR ($CD_2Cl_2$, $\delta$), 163.1, 163.0, 138.1, 137.8, 132.9, 132.5, 130.8, 130.4, 128.8, 128.7, 127.6, 127.3, 126.6, 126.4, 114.9, 114.7, 55.6, 38.2, 37.8, 33.4), 33.2, 28.9, 28.6 ppm. $^{31}$P NMR ($CD_2Cl_2$, $\delta$), 81.3 and 81.2 ppm. Mass spectrum ($CI^+$, $m/z$), 629 $[M + H]^+$. Accurate mass measurement [$CI^+$, $m/z$]: 629.0111 $[M + H]^+$, calculated mass for $C_{26}H_{30}O_2P_2S_6H$: 629.0118.

*4,11-Bis(4-methoxyphenyl)-3,5,10,12-tetrathia-4,11-diphospha-1(1,4)-benzenacyclotridecaphane 4,11-Disulfide* (***8***). White foam [0.598 g, 60% based on LR (1.6 mmol)]. Two diastereoisomers were



DOI: 10.1021/acs.joc.6b00573
J. Org. Chem. 2016, 81, 4210−4225

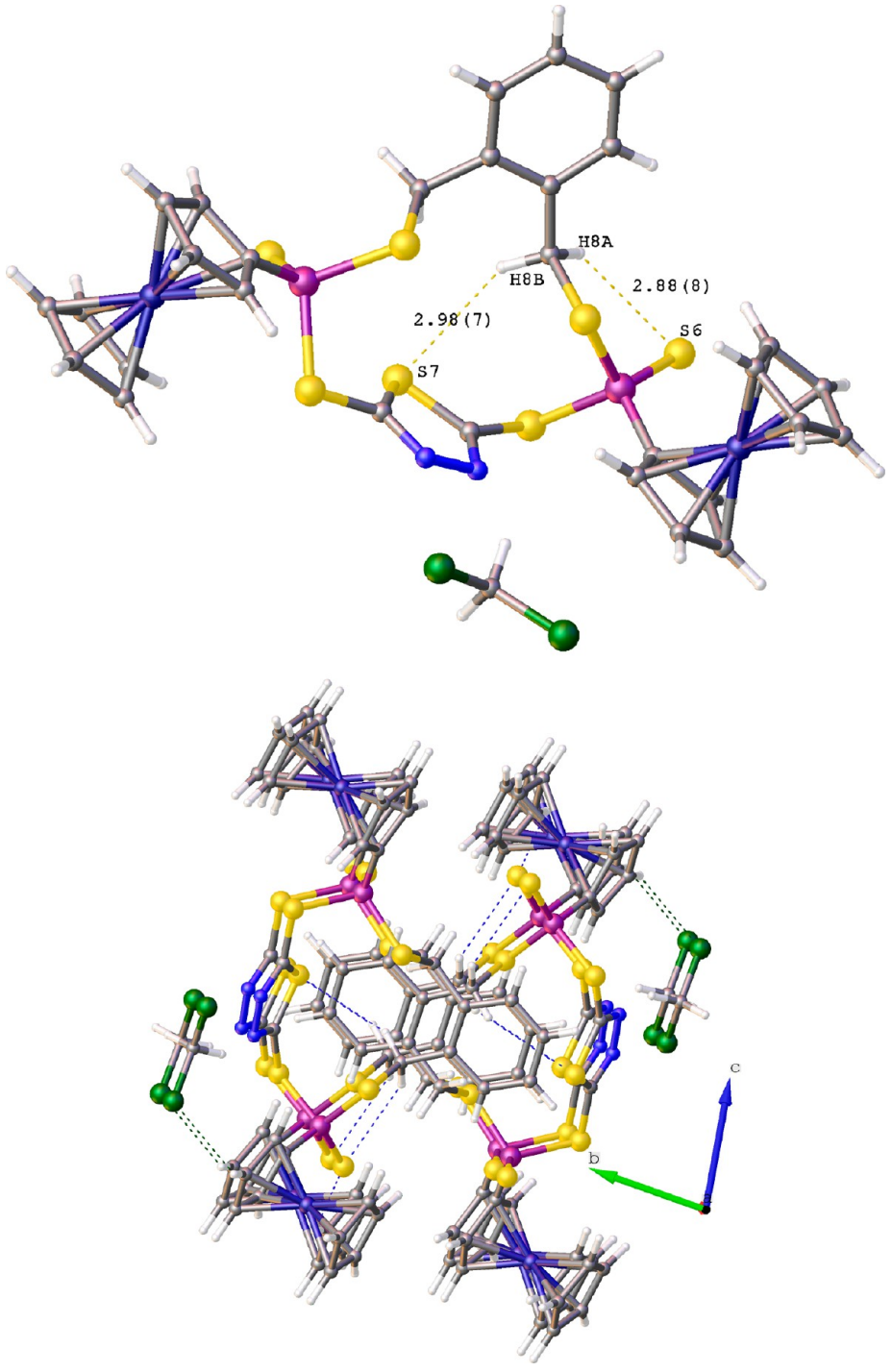



**Figure 7.** Upper diagram shows the intramolecular C(8)−H(8A)···S(6) and C(8)−H(8B)···S(7) hydrogen bonds [2.88(8) and 2.98(7) Å with the angle of 126.87° and 142.58°] in **19**. The lower diagram shows the intramolecular hydrogen bonds, intermolecular C−H···S and C−H···Cl short contacts, and $\pi$-stacking interactions in the supramolecular assembly of **19**.

found in ca. 2:1 intensity ratio. Selected IR (KBr, $cm^{-1}$): 1591(s), 1564(m), 1494(s), 1405(m), 1292(s), 1255(s), 1177(s), 1098(s), 1022(s), 826(m), 799(m), 683(s), 617(s), 534(s), 499(m), 447(m). $^1$H NMR ($CD_2Cl_2$, $\delta$), 7.88−7.81 (m, 8H), 7.33 (d, $J$(H,H) = 5.3 Hz, 4H), 7.13 (d, $J$(H,H) = 5.3 Hz, 4H), 6.94−6.90 (m, 8H), 4.36−4.23 (m, 4H), 4.03−3.88 (m, 4H), 3.77 (s, 6H), 3.76 (s, 6H), 2.87−2.32 (m, 8H), 1.65−1.54 (m, 4H), 1.40−1.28 (m, 4H) ppm. $^{13}$C NMR ($CD_2Cl_2$, $\delta$), 163.1, 163.0, 137.8, 137.7, 132.9, 132.7, 132.3, 132.2, 129.6, 129.4, 127.7, 126.7, 114.4, 114.2, 55.6, 38.2, 37.8, 33.4, 33.2, 28.9, 28.6 ppm. $^{31}$P NMR ($CD_2Cl_2$, $\delta$), 81.8 and 81.6 ppm. Mass spectrum (CI$^+$, $m/z$), 629 [M + H]$^+$. Accurate mass measurement [CI$^+$, $m/z$]: 629.0115 [M + H]$^+$, calculated mass for $C_{26}H_{30}O_2P_2S_6H$: 629.0118.

*3,9-Bis(4-methoxyphenyl)-2,4,8,10-tetrathia-3,9-diphospha-1-(2,5)-thiadiazola-6(1,4)-benzena-cyclodecaphane 3,9-Disulfide (**9**).* Off-white foam [0.719 g, 55% based on LR (2.0 mmol)]. Two diastereoisomers were found in ca. 2:1 intensity ratio. Selected IR (KBr, $cm^{-1}$): 1590(vs), 1564(m), 1495(s), 1459(m), 1407(m), 1295(m), 1258(vs), 1178(s), 1097(vs), 1022(s), 827(s), 800(m), 697(s), 617(m), 527(s), 445(m). $^1$H NMR ($CD_2Cl_2$, $\delta$), 7.94−7.73 (m, 8H), 7.28−7.05 (m, 16H), 6.93−6.80 (m, 8H), 4.38−3.97 (m, 8H), 3.75 (s, 6H), 3.74 (s, 6H) ppm. $^{13}$C NMR ($CD_2Cl_2$, $\delta$), 163.8,


DOI: 10.1021/acs.joc.6b00573
J. Org. Chem. 2016, 81, 4210−4225

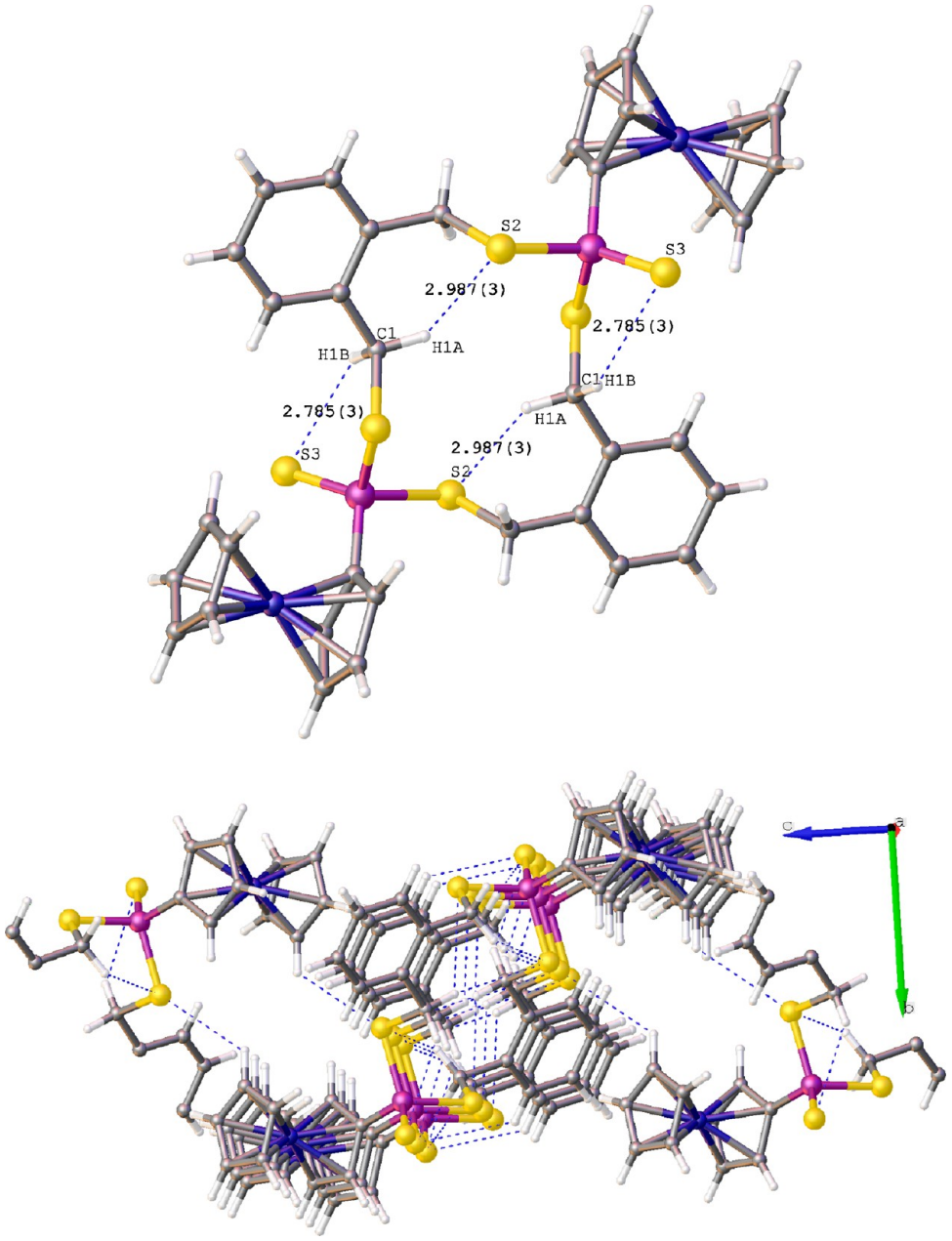



**Figure 8.** The upper diagram shows the intramolecular C(1)−H(1A)···S(2) and C(1)−H(1B)···S(3) hydrogen bonds [2.987(3) and 2.785(3) Å with the angles of 122.08° and 129.89°] in **22**. The lower diagram shows the intramolecular hydrogen bonds, intermolecular C−H···S short contacts, and $\pi$-stacking interactions in the supramolecular assembly of **22**.

163.7, 138.2, 138.1, 135.6, 135.4, 133.7, 133.3, 129.9, 129.6, 124.9, 124.0, 114.5, 114.4, 55.7, 55.6, 37.6, 37.5 ppm. $^{31}$P NMR ($CD_2Cl_2$, $\delta$), 80.0 and 79.6 ppm. Mass spectrum (EI$^+$, $m/z$), 656 [M]$^+$. Accurate mass measurement [EI$^+$, $m/z$]: 655.9195 [M]$^+$, calculated mass for $C_{24}H_{22}N_2O_2P_2S_7$: 655.9201.

*7,16-Bis(4-methoxyphenyl)-5,9,14,18-tetrahydrodibenzo[e,l]-[1,3,8,10]tetrathia[2,9]-diphosphacyclotetradecine 7,16-Disulfide (**10**).* White foam [0.45 g, 67% based on LR (1.0 mmol)]. Two diastereoisomers were found in ca. 1:3 intensity ratio. Selected IR (KBr, cm$^{-1}$): 1591(s), 1564(m), 1495(s), 1453(m), 1293(m), 1258(s), 1178(s), 1099(s), 1023(m), 827(m), 800(m), 766(m), 694(s), 618(m), 539(s), 502(m), 442(m). $^1$H NMR ($CD_2Cl_2$, $\delta$), 7.96−7.89 (m, 8H), 7.19−7.08 (m, 16H), 6.98−6.92 (m, 8H), 4.33−4.28 (m, 8H), 4.17−4.11 (m, 8H), 3.75 (s, 6H), 3.74 (s, 6H) ppm. $^{13}$C NMR ($CD_2Cl_2$, $\delta$), 163.5, 163.4, 140.2, 140.0, 134.3, 134.2, 133.0, 132.3, 131.5, 131.1), 129.0, 128.9, 114.7, 114.5, 55.7, 55.6, 36.1, 35.7 ppm. $^{31}$P NMR ($CD_2Cl_2$, $\delta$), 77.3 and 77.1 ppm. Mass spectrum (EI$^+$, $m/z$), 676 [M]$^+$. Accurate mass measurement [EI$^+$, $m/z$]: 676.0042 [M]$^+$, calculated mass for $C_{30}H_{30}O_2P_2S_6$: 676.0045.

**General Procedure for Preparation of Macrocycles 11−25.** A suspension of alkyldithiol or aryldithiol (2.0 mmol), sodium hydride (0.16 g, 60% suspension in oil, 4.0 mmol), FcLR (0.808 g, 2.0 mmol), and xylylene dibromide (0.528 g, 2.0 mmol) in dry THF (60 mL) was stirred at room temperature for 24 h, giving a reddish yellow or pale yellow suspension. Upon filtration to remove unreacted solid, the filtrate was dried in vacuo and the residue was dissolved in dichloromethane (10 mL). After removal of the salt by filtration, the liquid solution was concentrated to ca. 2 mL and was loaded onto a silica gel column (dichloromethane as eluent) to give compounds **12**−**25**. Another unexpected nine-membered ring **11** was also obtained yellow foam in respective 23%, 18%, 24%, and 23% yields for cases of **13**, **16**, **19**, and **22**.

*3-Ferrocenyl-1,5-dihydrobenzo[e][1,3,2]dithiaphosphepine 3-Sulfide (**11**).* Selected IR (KBr, cm$^{-1}$): 1491(m), 1440(m), 1409(m),



DOI: 10.1021/acs.joc.6b00573
J. Org. Chem. 2016, 81, 4210−4225

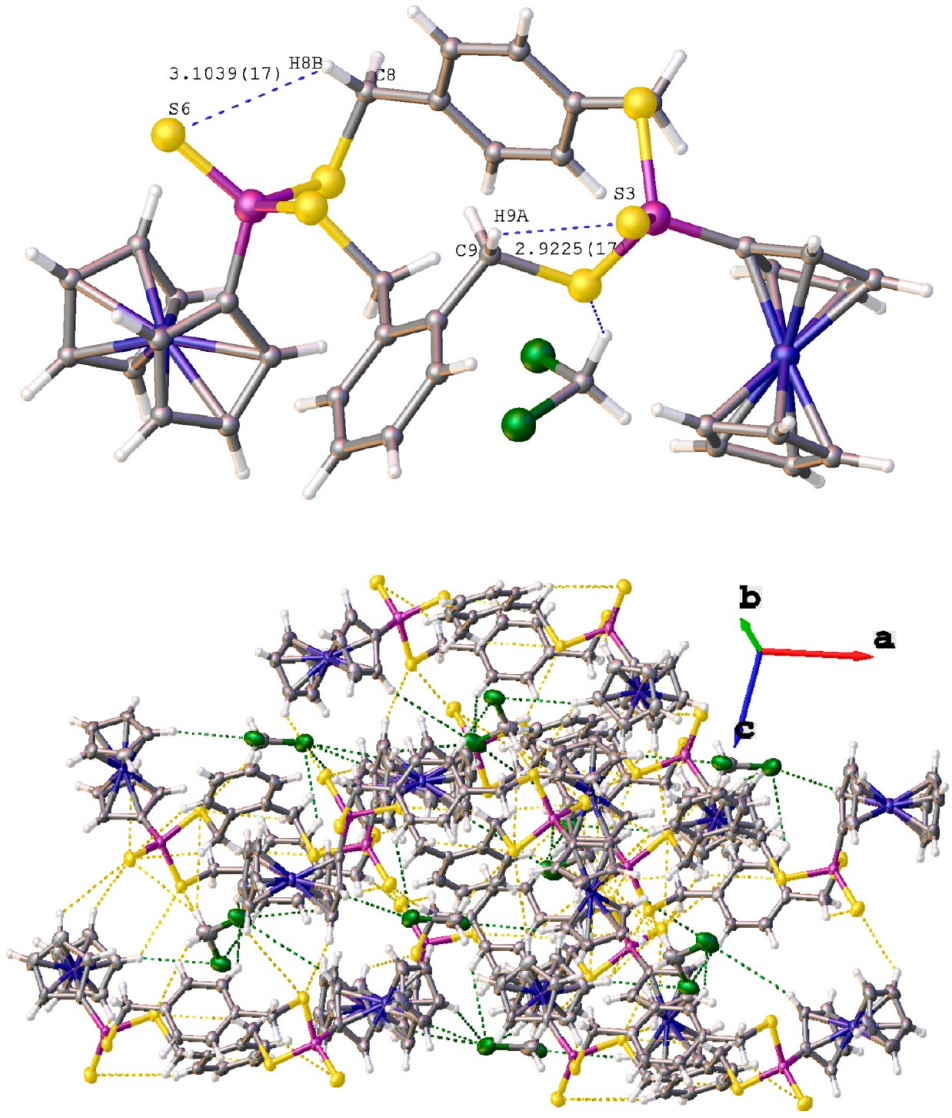



**Figure 9.** The upper diagram shows the intramolecular C(9)−H(9A)···S(3) and C(8)−H(8B)···S(6) hydrogen bonds [3.1039(17) and 2.9225(17) Å with the angles of 124.64° and 124.64°] in **24**. The lower diagram shows the intramolecular hydrogen bonds and intermolecular C−H···S and C−H···Cl short contacts in the supramolecular assembly of **24**.

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). $^{1}$H NMR ($CD_2Cl_2$, $\delta$), 7.25−7.19 (m, 4H), 4.76 (d, $J$(P,H) = 14.7 Hz, 1H), 4.72 (d, $J$(P,H) = 14.7 Hz, 1H), 4.50−4.43 (m, 2H), 4.30 (s, 5H), 3.91 (d, $J$(P,H) = 14.7 Hz, 2H), 3.85 (d, $J$(P,H) = 14.7 Hz, 2H) ppm. $^{13}$C NMR ($CD_2Cl_2$, $\delta$), 138.6, 130.0, 128.4, 73.7 (d, $J$(P,C) = 127 Hz), 72.2 (d, $J$(P,C) = 12.5 Hz), 70.9 (d, $J$(P,C) = 15.7 Hz), 70.5, 31.6 (d, $J$(P,C) = 2.6 Hz) ppm. $^{31}$P NMR ($CD_2Cl_2$, $\delta$), 50.2 ppm. Mass spectrum (EI$^+$, $m/z$), 416 [M]$^+$. Accurate mass measurement [EI$^+$, $m/z$]: 415.9568 [M]$^+$, calculated mass for $C_{18}H_{17}FePS_3$: 415.9574.

*4,9-Diferrocenyl-3,5,8,10-tetrathia-4,9-diphospha-1(1,4)-benzenacycloundecaphane 4,9-Disulfide (**12**).* Yellow foam [0.965 g, 64% based on FcLR (2.1 mmol)]. Two diastereoisomers were found in ca. 1:2 intensity ratio. Selected IR (KBr, cm$^{-1}$): 1510(m), 1409(m), 1170(s), 1105(m), 1023(s), 1001(m), 823(s), 674(vs), 529(m), 473(vs). $^{1}$H NMR ($CD_2Cl_2$, $\delta$), 7.54−7.30 (m, 8H), 4.65−4.54 (m, 16H), 4.37 (s, 10H), 4.36 (s, 10H), 4.29−4.02 (m, 8H), 3.30−3.12 (m, 8H) ppm. $^{13}$C NMR ($CD_2Cl_2$, $\delta$), 137.1, 136.2, 129.8, 129.6, 79.5 (d, $J$(P,C) = 105 Hz), 79.3 (d, $J$(P,C) = 105 Hz), 72.3 (d, $J$(P,C) = 11.8 Hz), 72.2 (d, $J$(P,C) = 12.0 Hz), 71.7 (d, $J$(P,C) = 15.0 Hz), 71.4 (d, $J$(P,C) = 14.9 Hz), 71.0, 70.9, 37.6, 37.3, 35.2, 33.9 ppm. $^{31}$P NMR ($CD_2Cl_2$, $\delta$), 81.9 and 81.8 ppm. Mass spectrum (EI$^+$, $m/z$), 756 [M]$^+$. Accurate mass measurement [EI$^+$, $m/z$]: 755.8847 [M]$^+$, calculated mass for $C_{30}H_{30}Fe_2P_2S_6$: 755.8840.

*3,9-Diferrocenyl-1,6,7,11-tetrahydro-5H-benzo[k][1,3,7,9]-tetrathia[2,8]diphosphacyclotridecine 3,9-Disulfide (**13**).* Yellow foam [1.35 g, 59% based on FcLR (3.0 mmol)]. Two diastereoisomers were found in ca. 1:4 intensity ratio. Selected IR (KBr, cm$^{-1}$): 1409(m), 1387(m), 1295(m), 1243(m), 1169(s), 1105(m), 1023(s), 1000(m), 822(s), 767(m), 673(vs), 617(m), 531(s), 476(vs). $^{1}$H NMR ($CD_2Cl_2$, $\delta$), 7.45−7.25 (m, 8H), 4.78−4.75 (m, 8H), 4.67−4.62 (m, 8H), 4.43 (s, 10H), 4.42 (s, 10H), 4.41−4.36 (m, 4H), 4.19−4.14 (m, 4H), 3.34−3.07 (m, 4H), 2.70−2.60 (m, 4H), 2.16−2.10 (m, 2H), 2.02−1.96 (m, 2H) ppm. $^{13}$C NMR ($CD_2Cl_2$, $\delta$), 134.4 (d, $J$(P,C) = 11.5 Hz), 134.3 (d, $J$(P,C) = 11.4 Hz), 131.6 (d, $J$(P,C) = 6.5 Hz), 128.8, 128.3, 78.6 (d, $J$(P,C) = 101 Hz), 78.5 (d, $J$(P,C) = 101 Hz), 72.1 (d, $J$(P,C) = 12.0 Hz), 72.0 (d, $J$(P,C) = 11.8 Hz), 71.5 (d, $J$(P,C) = 15.0 Hz), 71.3 (d, $J$(P,C) = 14.7 Hz), 70.9, 70.8, 35.6, 35.2, 32.5, 32.1, 29.0, 28.9 ppm. $^{31}$P NMR ($CD_2Cl_2$, $\delta$), 79.5 and 79.1 ppm. Mass spectrum (EI$^+$, $m/z$), 770 [M]$^+$. Accurate mass measurement [EI$^+$, $m/z$]: 769.9004 [M]$^+$, calculated mass for $C_{31}H_{32}Fe_2P_2S_6$: 769.8997.

*4,10-Diferrocenyl-3,5,9,11-tetrathia-4,10-diphospha-1(1,3)-benzenacyclododecaphane 4,10-Disulfide (**14**).* Yellow foam [1.274 g, 55% based on FcLR (3.0 mmol)]. Two diastereoisomers were found



DOI: 10.1021/acs.joc.6b00573
J. Org. Chem. 2016, 81, 4210−4225

in ca. 2:1 intensity ratio. Selected IR (KBr, $cm^{-1}$): 1483(m), 1408(m), 1253(m), 1169(s), 1105(m), 1023(s), 1000(m), 822(s), 705(m), 674(vs), 617(m), 528(s), 475(vs). $^1H$ NMR ($CD_2Cl_2$, $\delta$), 7.21−7.16 (m, 8H), 4.59−4.53 (m, 8H), 4.47−4.42 (m, 8H), 4.30 (s, 10H), 4.27 (s, 10H), 4.25−4.19 (m, 4H), 4.08−3.97 (m, 4H), 2.76−2.65 (m, 4H), 2.55−2.49 (m, 4H), 1.79−1.72 (m, 4H) ppm. $^{13}C$ NMR ($CD_2Cl_2$, $\delta$), 138.6, 138.4, 130.2, 130.1, 129.0, 128.6, 128.4, 128.3, 80.0 (d, $J$(P,C) = 102 Hz), 79.9 (d, $J$(P,C) = 102 Hz), 72.1 (d, $J$(P,C) = 11.8 Hz), 72.0 (d, $J$(P,C) = 11.8 Hz), 71.5 (d, $J$(P,C) = 14.5 Hz), 71.4 (d, $J$(P,C) = 14.6 Hz), 70.9, 70.8, 37.7 (d, $J$(P,C) = 19.0 Hz), 37.6 (d, $J$(P,C) = 19.0 Hz), 32.9 (d, $J$(P,C) = 42.1 Hz), 32.8 (d, $J$(P,C) = 42.1 Hz), 29.4, 29.3 ppm. $^{31}P$ NMR ($CD_2Cl_2$, $\delta$), 83.1 and 83.0 ppm. Mass spectrum ($EI^+$, $m/z$), 770 $[M]^+$. Accurate mass measurement [$EI^+$, $m/z$]: 769.8998 $[M]^+$, calculated mass for $C_{31}H_{32}Fe_2P_2S_6$: 769.8997.

*4,10-Diferrocenyl-3,5,9,11-tetrathia-4,10-diphospha-1(1,4)-benzenacyclododecaphane 4,10-Disulfide* (**15**). Yellow foam [0.89 g, 58% based on FcLR (2.0 mmol)]. Two diastereoisomers were found in ca. 9:1 intensity ratio. Selected IR (KBr, $cm^{-1}$): 1409(m), 1387(m), 1363(m), 1300(m), 1236(m), 1300(m), 1236(m), 1174(s), 1102(m), 1024(s), 998(m), 821(s), 672(vs), 618(m), 530(s), 490(s), 472(s). $^1H$ NMR ($CD_2Cl_2$, $\delta$), 7.36−7.21 (m, 8H), 4.46−4.42 (m, 16H), 4.29 (s, 10H), 4.28 (s, 10H), 4.27−4.21 (m, 4H), 4.06−3.94 (m, 4H), 2.37−2.16 (m, 8H), 1.74−1.47 (m, 4H) ppm. $^{13}C$ NMR ($CD_2Cl_2$, $\delta$), 138.1, 137.9, 129.7, 129.6, 79.9 (d, $J$(P,C) = 103 Hz), 79.6 (d, $J$(P,C) = 103 Hz), 72.0 (d, $J$(P,C) = 11.6 Hz), 71.9 (d, $J$(P,C) = 11.6 Hz), 71.4 (d, $J$(P,C) = 14.7 Hz), 71.1 (d, $J$(P,C) = 14.7 Hz), 70.9, 70.8, 37.5, 37.4, 32.2, 31.9, 28.1, 28.0 ppm. $^{31}P$ NMR ($CD_2Cl_2$, $\delta$), 81.5 and 81.2 ppm. Mass spectrum ($EI^+$, $m/z$), 770 $[M]^+$. Accurate mass measurement [$EI^+$, $m/z$]: 765.9087 $[M]^+$, calculated mass for $C_{31}H_{32}{}^{54}Fe_2P_2S_6$: 765.9090.

*3,10-Diferrocenyl-1,5,6,7,8,12-hexahydrobenzo[e][1,3,8,10]-tetrathia[2,9]diphosphacyclotetradecine 3,10-Disulfide* (**16**). Yellow foam [0.53 g, 45% based on FcLR (2.0 mmol)]. Two diastereoisomers were found in ca. 1:6 intensity ratio. Selected IR (KBr, $cm^{-1}$): 1409(m), 1305(m), 1239(m), 1170(s), 1105(m), 1024(s), 1002(m), 951(m), 822(s), 765(m), 676(vs), 532(m), 477(vs). $^1H$ NMR ($CD_2Cl_2$, $\delta$), 7.22−7.14 (m, 8H), 4.64−4.60 (m, 8H), 4.50−4.47 (m, 8H), 4.31 (s, 10H), 4.30 (s, 10H), 4.27−4.25 (m, 4H), 4.23−4.19 (m, 4H), 4.02−3.96 (m, 4H), 3.04−2.96 (m, 4H), 1.92−1.18 (m, 8H) ppm. $^{13}C$ NMR ($CD_2Cl_2$, $\delta$), 135.0, 134.9, 131.6, 131.5, 128.9, 128.7, 79.2 (d, $J$(P,C) = 101 Hz), 79.1 (d, $J$(P,C) = 101 Hz), 72.4 (d, $J$(P,C) = 12.1 Hz), 72.3 (d, $J$(P,C) = 12.1 Hz), 71.8 (d, $J$(P,C) = 14.7 Hz), 71.7 (d, $J$(P,C) = 14.7 Hz), 71.3, 71.2, 35.8, 35.6, 32.8, 32.7, 27.7, 27.6 ppm. $^{31}P$ NMR ($CD_2Cl_2$, $\delta$), 80.4 and 80.2 ppm. Mass spectrum ($EI^+$, $m/z$), 784 $[M]^+$. Accurate mass measurement [$EI^+$, $m/z$]: 783.9149 $[M]^+$, calculated mass for $C_{32}H_{34}Fe_2P_2S_6$: 783.9153.

*4,11-Diferrocenyl-3,5,10,12-tetrathia-4,11-diphospha-1(1,3)-benzenacyclotridecaphane 4,11-Disulfide* (**17**). Sticky reddish yellow solid [0.685 g, 56% based on FcLR (1.56 mmol)]. Two diastereoisomers were found in ca. 2:5 intensity ratio. Selected IR (KBr, $cm^{-1}$): 1408(m), 1306(m), 1235(m), 1168(s), 1105(m), 1022(s), 10000(m), 820(s), 704(s), 672(vs), 616(m), 528(s), 474(vs). $^1H$ NMR ($CD_2Cl_2$, $\delta$), 7.49 (s, 1H), 7.44 (s, 1H), 7.30−7.16 (m, 6H), 4.60−4.52 (m, 8H), 4.47−4.42 (m, 8H), 4.30 (s, 10H), 4.27 (s, 10H), 4.19−4.10 (m, 4H), 4.08−3.98 (m, 4H), 2.81−2.75 (m, 4H), 2.47−2.42 (m, 4H), 1.77−1.30 (m, 8H) ppm. $^{13}C$ NMR ($CD_2Cl_2$, $\delta$), 138.3, 138.2, 130.3, 130.1, 129.0, 128.7, 128.5, 128.4, 80.2 (d, $J$(P,C) = 101.0 Hz), 80.1 (d, $J$(P,C) = 101.5 Hz), 71.9 (d, $J$(P,C) = 12.0 Hz), 71.5, 71.4, 71.3, 70.9, 70.8, 38.1, 37.8, 33.0, 32.8, 28.7, 28.4 ppm. $^{31}P$ NMR ($CD_2Cl_2$, $\delta$), 82.1 and 82.0 ppm. Mass spectrum ($CI^+$, $m/z$), 785 $[M + H]^+$. Accurate mass measurement [$CI^+$, $m/z$]: 782.9275 $[M + H]^+$, calculated mass for $C_{32}H_{34}{}^{54}FeFeP_2S_6H$: 782.9278.

*4,11-Diferrocenyl-3,5,10,12-tetrathia-4,11-diphospha-1(1,4)-benzenacyclotridecaphane 4,11-Disulfide* (**18**). Yellow foam [0.666 g, 49% based on FcLR (1.75 mmol)]. Two diastereoisomers were found in ca. 2:3 intensity ratio. Selected IR (KBr, $cm^{-1}$): 1510(m), 1409(m), m1238(m), 1169(s), 1105(m), 1023(s), 1002(m), 822(s), 673(vs), 529(m), 475(vs). $^1H$ NMR ($CD_2Cl_2$, $\delta$), 7.33−7.21 (m, 8H), 4.66−4.52 (m, 8H), 4.48−4.42 (m, 8H), 4.30 (s, 10H), 4.29 (s, 10H), 4.28−4.07 (m, 4H), 3.93−3.56 (m, 4H), 2.87−2.76 (m, 4H), 2.47−2.28 (m, 4H), 1.76−1.59 (m, 4H), 1.35−1.18 (m, 4H) ppm. $^{13}C$ NMR ($CD_2Cl_2$, $\delta$), 138.0, 137.9, 129.6, 129.3, 79.7 (d, $J$(P,C) = 102.6 Hz), 79.6 (d, $J$(P,C) = 102.1 Hz), 72.0, 71.9, 71.6), 71.3, 70.9, 70.8, 37.6, 37.2, 33.0, 32.6, 29.0, 28.5 ppm. $^{31}P$ NMR ($CD_2Cl_2$, $\delta$), 82.7 and 82.6 ppm. Mass spectrum ($CI^+$, $m/z$), 785 $[M + H]^+$. Accurate mass measurement [$CI^+$, $m/z$]: 782.9279 $[M + H]^+$, calculated mass for $C_{32}H_{34}{}^{54}FeFeP_2S_6H$: 782.9278.

*3,9-Diferrocenyl-2,4,8,10-tetrathia-3,9-diphospha-1(2,5)-thiadiazola-6(1,2)-benzenacyclodecaphane 3,9-Disulfide* (**19**). Dark yellow foam [1.073 g, 66% based on FcLR (2.0 mmol)]. Two diastereoisomers were found in ca. 1:1 intensity ratio. Selected IR (KBr, $cm^{-1}$): 1489(m), 1450(m), 1409(m), 1339(m), 1237(m), 1174(s), 1027(s), 951(m), 825(s), 767(m), 689(vs), 534(m), 486(vs), 467(vs). $^1H$ NMR ($CD_2Cl_2$, $\delta$), 7.27−7.13 (m, 16H), 4.79−4.74 (m, 8H), 4.60−4.58 (m, 8H), 4.38 (s, 10H), 4.37 (s, 10H), 4.34−4.21 (m, 4H), 4.01−3.97 (m, 4H) ppm. $^{13}C$ NMR ($CD_2Cl_2$, $\delta$), 162.5, 161.6, 134.5, 134.2, 131.6, 131.5, 129.5, 129.1, 75.1 (d, $J$(P,C) = 89 Hz), 74.9 (d, $J$(P,C) = 88 Hz), 72.7, 72.4, 71.6, 71.4, 71.0, 70.9, 38.6, 37.4 ppm. $^{31}P$ NMR ($CD_2Cl_2$, $\delta$), 82.3 and 82.2 ppm. Mass spectrum ($EI^+$, $m/z$), 812 $[M]^+$. Accurate mass measurement [$EI^+$, $m/z$]: 811.8315 $[M]^+$, calculated mass for $C_{30}H_{26}N_2Fe_2P_2S_7$: 811.8313.

*3,9-Diferrocenyl-2,4,8,10-tetrathia-3,9-diphospha-1(2,5)-thiadiazola-6(1,3)-benzenacyclodecaphane 3,9-Disulfide* (**20**). Golden foam [0.795 g, 49% based on FcLR (2.0 mmol)]. Two diastereoisomers were found in ca. 2:3 intensity ratio. Selected IR (KBr, $cm^{-1}$): 1408(m), 1364(m), 1317(m), 1227(m), 1172(s), 1106(m), 1026(vs), 896(m), 824(s), 686(vs), 532(m), 485(vs), 463(vs). $^1H$ NMR ($CD_2Cl_2$, $\delta$), 7.42 (s, 1H), 7.41 (s, 1H), 7.24−7.20 (m, 10H), 7.17−7.15 (m, 4H), 4.77−4.69 (m, 8H), 4.61−4.55 (m, 8H), 4.34 (s, 10H), 4.32 (s, 10H), 4.29−4.03 (m, 8H) ppm. $^{13}C$ NMR ($CD_2Cl_2$, $\delta$), 160.9, 160.6, 138.2, 137.8, 131.3, 131.0, 128.8, 128.7, 128.2, 128.1, 79.9 (d, $J$(P,C) = 103 Hz), 79.8 (d, $J$(P,C) = 104 Hz), 72.9 (d, $J$(P,C) = 12.6 Hz), 72.8 (d, $J$(P,C) = 12.9 Hz), 72.3 (d, $J$(P,C) = 12.6 Hz), 72.0 (d, $J$(P,C) = 13.0 Hz), 71.0, 70.9, 38.6, 38.0 ppm. $^{31}P$ NMR ($CD_2Cl_2$, $\delta$), 85.8 and 83.6 ppm. Mass spectrum ($EI^+$, $m/z$), 812 $[M]^+$. Accurate mass measurement [$EI^+$, $m/z$]: 811.8307 $[M]^+$, calculated mass for $C_{30}H_{26}N_2Fe_2P_2S_7$: 811.8313.

*3,9-Diferrocenyl-2,4,8,10-tetrathia-3,9-diphospha-1(2,5)-thiadiazola-6(1,4)-benzen-acyclodecaphane 3,9-Disulfide* (**21**). Reddish orange foam [0.748 g, 46% based on FcLR (2.0 mmol)]. Two diastereoisomers were found in ca. 2:1 intensity ratio. Selected IR (KBr, $cm^{-1}$): 1510(m), 1409(m), 1364(m), 1310(m), 1239(m), 171(s), 1105(m), 1024(s), 823(s), 683(vs), 615(m), 533(m), 486(vs), 459(vs). $^1H$ NMR ($CD_2Cl_2$, $\delta$), 7.26−7.20 (m, 16H), 4.76−4.71 (m, 8H), 4.56−4.50 (m, 8H), 4.36 (s, 10H), 4.33 (s, 10H), 4.32−4.22 (m, 8H) ppm. $^{13}C$ NMR ($CD_2Cl_2$, $\delta$), 160.9, 160.8, 137.7, 137.6, 130.1, 130.0, 129.9, 129.6, 129.5, 129.4, 78.1 (d, $J$(P,C) = 105 Hz), 77.9 (d, $J$(P,C) = 103 Hz), 72.9 (d, $J$(P,C) = 12.8 Hz), 72.8 (d, $J$(P,C) = 13.0 Hz), 72.4 (d, $J$(P,C) = 16.0 Hz), 72.3 (d, $J$(P,C) = 15.1 Hz), 71.1, 71.0, 38.1, 36.9 ppm. $^{31}P$ NMR ($CD_2Cl_2$, $\delta$), 83.3 and 82.8 ppm. Mass spectrum ($EI^+$, $m/z$), 812 $[M]^+$. Accurate mass measurement [$EI^+$, $m/z$]: 811.8313 $[M]^+$, calculated mass for $C_{30}H_{26}N_2Fe_2P_2S_7$: 811.8313.

*7,16-Diferrocenyl-5,9,14,18-tetrahydrodibenzo[e,l][1,3,8,10]-tetrathia[2,9]-diphosphacyclotetradecine 7,16-Disulfide* (**22**). Yellow solid [0.492 g, 59% based on FcLR (1.0 mmol)]. Two diastereoisomers were found in ca. 2:1 intensity ratio. Selected IR (KBr, $cm^{-1}$): 1490(m), 1452(m), 1173(s), 1106(m), 1025(s), 1002(m), 821(s), 767(s), 696(s), 672(vs), 533(s), 478(vs). $^1H$ NMR ($CD_2Cl_2$, $\delta$), 7.26−7.19 (m, 16H), 4.68−4.67 (m, 8H), 4.53−4.51 (m, 8H), 4.31 (s, 10H), 4.30 (s, 10H), 4.28−4.23 (m, 8H), 4.10−4.06 (m, 8H) ppm. $^{13}C$ NMR ($CD_2Cl_2$, $\delta$), 134.5, 134.4, 131.5, 131.4, 128.9, 128.8, 77.6 (d, $J$(P,C) = 99 Hz), 77.5 (d, $J$(P,C) = 101 Hz), 72.3 (d, $J$(P,C) = 12.0 Hz), 72.1 (d, $J$(P,C) = 11.9 Hz), 71.4 (d, $J$(P,C) = 15.0 Hz), 71.3 (d, $J$(P,C) = 14.9 Hz), 71.0, 70.8, 35.3, 35.2 ppm. $^{31}P$ NMR ($CD_2Cl_2$, $\delta$), 78.2 and 78.0 ppm. Mass spectrum ($EI^+$, $m/z$), 832 $[M]^+$. Accurate mass measurement [$EI^+$, $m/z$]: 831.9157 $[M]^+$, calculated mass for $C_{36}H_{34}Fe_2P_2S_6$: 831.9159.

*4,10-Diferrocenyl-3,5,9,11-tetrathia-4,10-diphospha-1(1,2),7-(1,3)-dibenzenacyclododecaphane 4,10-Disulfide* (**23**). Yellow foam



DOI: 10.1021/acs.joc.6b00573
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[0.535 g, 64% based on FcLR (1.0 mmol)]. Two diastereoisomers were found in ca. 8:1 intensity ratio. Selected IR (KBr, $cm^{-1}$): 1485(m), 1444(m), 1408(m), 1305(m), 1168(s), 1105(m), 1022(s), 821(s), 762(m), 668(vs), 616(m), 526(s), 472(vs). $^1H$ NMR ($CD_2Cl_2$, $\delta$), 7.60 (s, 1H), 7.57 (s, 1H), 7.27−7.06 (m, 14H), 4.65−4.56 (m, 8H), 4.48−4.44 (m, 8H), 4.29 (s, 10H), 4.28 (s, 10H), 4.14−4.05 (m, 8H), 3.89−3.37 (m, 8H) ppm. $^{13}C$ NMR ($CD_2Cl_2$, $\delta$), 139.0, 138.9, 138.8, 138.3, 135.3, 130.9, 130.7, 130.1, 129.8, 128.7, 128.6, 128.4, 128.3, 79.0 (d, $J$(P,C) = 101 Hz), 78.7 (d, $J$(P,C) = 103 Hz), 72.4 (d, $J$(P,C) = 11.8 Hz), 72.3 (d, $J$(P,C) = 11.4 Hz), 71.7 (d, $J$(P,C) = 15.0 Hz), 71.6 (d, $J$(P,C) = 14.9 Hz), 71.1, 71.0, 37.6, 37.2, 35.1, 34.8 ppm. $^{31}P$ NMR ($CD_2Cl_2$, $\delta$), 81.6 and 80.2 ppm. Mass spectrum (EI$^+$, $m/z$), 832 [M]$^+$. Accurate mass measurement [EI$^+$, $m/z$]: 831.9155 [M]$^+$, calculated mass for $C_{36}H_{34}Fe_2P_2S_6$: 831.9159.

*4,10-Diferrocenyl-3,5,9,11-tetrathia-4,10-diphospha-1(1,2),7-(1,4)-dibenzenacyclododecaphane 4,10-Disulfide (**24**).* Orange foam [0.468 g, 56% based on FcLR (1.0 mmol)]. Two diastereoisomers were found in ca. 3:1 intensity ratio. Selected IR (KBr, $cm^{-1}$): 1409(m), 1239(m), 1170(s), 111(m), 1024(s), 823(s), 772(m), 736(m), 674(vs), 529(m), 476(vs). $^1H$ NMR ($CD_2Cl_2$, $\delta$), 7.22−7.12 (m, 8H), 7.03−6.98 (m, 8H), 4.67−4.62 (m, 8H), 4.54−4.49 (m, 8H), 4.30 (s, 10H), 4.29 (s, 10H), 4.07−3.93 (m, 4H), 3.77−3.70 (m, 4H), 3.63−3.57 (m, 4H), 3.26−3.10 (m, 4H) ppm. $^{13}C$ NMR ($CD_2Cl_2$, $\delta$), 137.6, 137.3, 135.1, 135.0, 131.2, 130.7, 129.8, 129.3, 128.2, 127.8, 78.6 (d, $J$(P,C) = 103 Hz), 78.5 (d, $J$(P,C) = 102 Hz), 72.3 (d, $J$(P,C) = 11.9 Hz), 72.2 (d, $J$(P,C) = 12.0 Hz), 71.6 (d, $J$(P,C) = 15.0 Hz), 71.5 (d, $J$(P,C) = 15.0 Hz), 71.0, 70.9, 37.6, 37.2, 36.2, 35.1 ppm. $^{31}P$ NMR ($CD_2Cl_2$, $\delta$), 81.9 and 81.7 ppm. Mass spectrum (EI$^+$, $m/z$), 832 [M]$^+$. Accurate mass measurement [EI$^+$, $m/z$]: 831.9156 [M]$^+$, calculated mass for $C_{36}H_{34}Fe_2P_2S_6$: 831.9159.

*2,9-Diferrocenyl-1,3,8,10-tetrathia-2,9-diphosphacyclooctadecane 2,9-Disulfide (**25**).* Reddish yellow paste [0.630 g, 46% based on FcLR (1.75 mmol)]. Selected IR (KBr, $cm^{-1}$): 1433(m), 1409(m), 1247(m), 1171(s), 1106(m), 1024(s), 1000(m), 824(s), 678(vs), 533(m), 480(s). $^1H$ NMR ($CD_2Cl_2$, $\delta$), 4.55−4.53 (m, 4H), 4.44−4.42 (m, 4H), 4.28 (s, 10H), 3.34 (t, $J$(H,H) = 6.8 Hz, 4H), 2.94−2.72 (m, 8H), 2.49−2.41 (m, 4H), 1.81−1.54 (m, 4H), 1.35−1.22 (m, 4H) ppm. $^{13}C$ NMR ($CD_2Cl_2$, $\delta$), 81.1 (d, $J$(P,C) = 101.4 Hz), 72.1 (d, $J$(P,C) = 11.7 Hz), 71.7 (d, $J$(P,C) = 14.9 Hz), 71.1, 34.6, 33.2, 34.6, 30.3, 29.5, 28.4, 24.4 ppm. $^{31}P$ NMR ($CD_2Cl_2$, $\delta$), 81.6 ppm. Mass spectrum (EI$^+$, $m/z$), 792 [M]$^+$. Accurate mass measurement [EI$^+$, $m/z$]: 791.9777 [M]$^+$, calculated mass for $C_{32}H_{42}Fe_2P_2S_6$: 791.9779.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00573.

X-ray data (ZIP)

Copies of $^1H$ and $^{13}C$ NMR spectra of compounds **1**−**25** and ORTEP plots of X-ray structures of compounds **5**, **10**, **15**, **18**, **19**, **22**, and **24** (PDF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We are grateful to the University of St. Andrews for financial support and the EPSRC National Mass Spectrometry Service Centre (Swansea) for mass spectral measurements.

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