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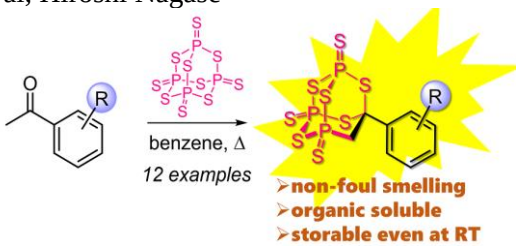

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Synthesis of heterocyclic compounds with adamantane-like cage structures consisting of phosphorus, sulfur, and carbon

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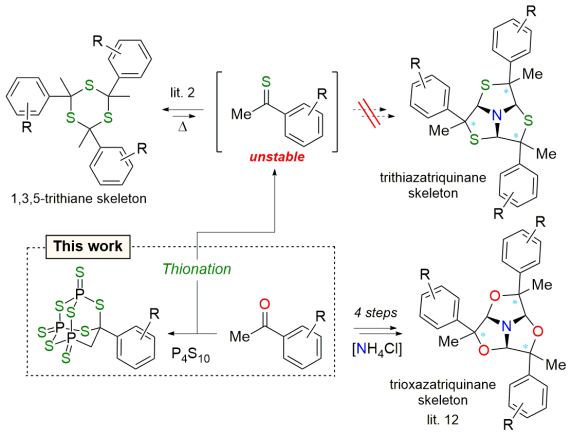
ABSTRACT

The synthesis of novel adamantane-like cage compounds consisting of phosphorus, sulfur, and carbon atoms was developed. We examined the reaction of a variety of acetophenone derivatives with P_4S_{10} in refluxing benzene. A novel noradamantane-like cage compound was also synthesized, when the reaction of 2'-methoxyacetophenone with P_4S_{10} was performed in refluxing toluene. In addition, by using the adamantane-like cage compound, 4,4'-dimethoxybenzophenone and *N*,*N*-dimethylbenzamide were successfully transformed into the corresponding thioketone (98%) and benzothioamide (89%), respectively.

1. Introduction

Thiocarbonyl compounds are useful and attractive tools for organic synthesis, especially as reactive synthetic intermediates,[1] even though such compounds are generally unstable. The structurally simple building block thioacetophenone is quite unstable in the monomeric form and can exist in a cyclic trimeric form, that is, 2,4,6-trimethyl-2,4,6-triphenyl-1,3,5-trithiane.[2] In another instance, Motoki and coworkers reported that the thionation of chalcone with tetraphosphorus decasulfide (P_4S_{10}, Berzelius reagent)[3] in carbon disulfide proceeded readily to give the corresponding thione dimer in moderate yield.[4] On the other hand, experimental and theoretical observations have indicated that neighboring group effects influenced the stability and the reactivity of the thiocarbonyl group.[5-7] Moreover, the electronic effects of the neighboring functional groups,[8] such as the 4,4'-bis(*N*,*N*-dimethylamino)phenyl group of thio-Michler's ketone,[8c] have also been involved in the stability of the thiocarbonyl group.

The choice of thionating agent is also particularly essential for the study of thiocarbonyl compounds. The representative thionating agents in organic synthesis are P_4S_{10}[3] and Lawesson's reagent (LR)[9], and the latter has tended to be used more frequently due to its broad solubility and better yields of the products. At present, the thionation mechanism of both reagents and their related derivatives[10] are not completely clear, although it has been generally accepted that the dithiophosphine ylides (R-PS_2) generated *in situ* upon heating are the reactive species.[3a,8b,11]



Scheme 1. Synthesis of 1,3,5-trioxazatriquinane compounds and the discovery of novel adamantane-like cage structures.

Recently, we reported the effective synthesis of 1,3,5-trioxazatriquinane skeletons from the corresponding acetophenones and their curious opioid receptor agonistic activities.[12] Based on this research background, we envisioned the design and synthesis of 1,3,5-trithiazatriquinane derivatives from the corresponding thioacetophenones generated *in situ*. However, we found that the thionating conditions of acetophenone derivatives with P_4S_{10} formed an unprecedented adamantane-like cage structure consisting of phosphorus, sulfur, and carbon atoms (Scheme 1). In addition, the adamantane-like

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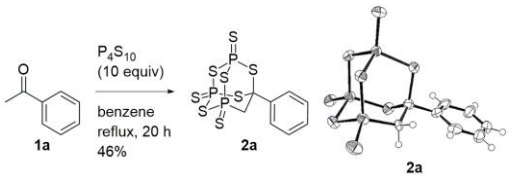
compound showed a good thionating ability. We describe herein the details of our findings.

2. Results and discussion

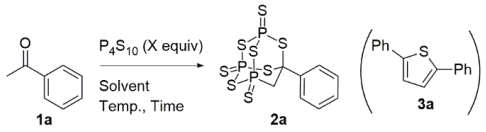
The reaction of acetophenone (**1a**) with 10 equivalents of P_4S_{10} for 20 hours in refluxing benzene followed by recrystallization from chloroform gave a colorless crystal. The ^{1}H NMR and ^{13}C NMR spectra of the unknown compound suggested the disappearance of a methyl group and a connection between a phosphorus and a carbon. The ^{31}P NMR spectrum showed the existences of two equivalent phosphorus atoms and another phosphorus atom at 56.7, 62.0 ppm, respectively. Finally, X-ray crystallography revealed the structure of the unknown compound as a novel adamantane-like cage compound **2a** (Scheme 2).[13] Intriguingly, in terms of the structural features, the reactive PS_2 moiety was removed from P_4S_{10}, and the acetyl group of **1a** seemed to be embedded into the site of the residual P_3S_8. As for physical properties, the adamantane-like cage compound **2a** was sensitive to polar solvents such as THF, DMF, acetone, methanol, and DMSO, although **2a** was fairly stable and storable at room temperature for at least 2 months under an argon atmosphere.



Scheme 2. Synthesis of **2a** and the X-ray structure of **2a**.

To gain insight into the formation of **2a**, we attempted to optimize the reaction conditions using **1a** (Table 1). The yield of **2a** was similar when the reaction was carried out under reflux in either benzene or toluene (Entries 1 and 2). However, the formation of **2a** and the decomposition of **2a** proceeded simultaneously as indicated by TLC analysis when toluene was used. In addition, the product **2a** seemed to gradually decompose at high temperature (Entries 2 and 3), and halogen solvents were also unsuitable for this reaction (Entries 4 and 5). Therefore, benzene was selected as the solvent of choice. With regards to the reaction time, the yield of **2a** was gradually increased over time, even though the starting material **1a** was consumed without a trace within one hour (Entries 1 and 6). However, prolonged reaction time led to the decomposition of **2a** (Entry 7). When 1.0 equivalent of P_4S_{10} was used, the reaction gave only trace amounts of the desired **2a** together with 2,5-diphenylthiophene (**3a**) in 16% yield as a by-product (Entry 8).[14] In contrast, when 5.0 equivalents of P_4S_{10} was used, the yield of **2a** was comparable to that of Entry 1 (Entry 9). In addition, the temperature was also a critical factor for this reaction; the formation of **2a** barely proceeded even at 60 °C (Entries 10 and 11). A short silica gel column chromatography before recrystallization led to the stable yield of **2a** (Entry 1, 46% yield in parentheses). This outcome indicated that **2a** and the similar derivatives **2** were rather stable toward silica gel column chromatography and we could, therefore, select the appropriate purification methods depending on the type of products formed.

Table 1
Optimization of reaction conditions.

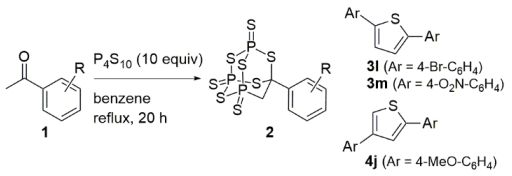


Entry	Solvent	X (equiv)	Temp (°C)	Time (h)	Yield (%)[a]
1	Benzene	10	Reflux	20	46 (46)[b]
2	Toluene	10	Reflux	20	52
3	Xylene	10	Reflux	20	9
4	CCl_4	10	Reflux	20	19
5	$(CH_2Cl)_2$	10	Reflux	20	27
6	Benzene	10	Reflux	4	26
7	Benzene	10	Reflux	60	37
8	Benzene	1	Reflux	20	trace[c]
9	Benzene	5	Reflux	20	42
10	Benzene	10	RT	20	trace
11	Benzene	10	60	20	4

[a] Isolated yield through recrystallization from chloroform.
[b] Isolated yield through a short silica gel column with chloroform followed by recrystallization from chloroform.
[c] **3a** was isolated (16%).

After establishing the optimized reaction conditions, we examined the generality of this promising reaction using a variety of acetophenone derivatives **1** and P_4S_{10} (Table 2). Although all reaction systems could not be monitored by TLC due to the presence of multiple spots, the simple purification operation (short column chromatography followed by recrystallization, or recrystallization alone) gave the corresponding adamantane-like cage compounds **2** easily. The tendencies of these reactions were as follows: (i) the reactions of 2'-substituted **1b**, **1c**, and **1d** gave **2b**, **2c**, and **2d**, respectively, in relatively low yields, although the reaction of **1e** gave no detectable compounds (Entries 1–4); (ii) the reactions of 3'-substituted acetophenones, with the exception of **1h**, gave the corresponding **2** in relatively high yields (Entries 5–8); (iii) the reactions of 4'-substituted **1j**, **1l**, and **1m** generated 2,4-bis(4-methoxyphenyl)thiophene (**4j**),[15] 2,5-bis(4-bromophenyl)thiophene (**3l**),[14b,14c,14e,14h] and 2,5-bis(4-nitrophenyl)thiophene (**3m**),[16] respectively (Entries 9, 11, and 12). All the NMR spectra of these derivatives **2b–2m** corresponded to that of **2a**. Interestingly, the ^{31}P NMR showed the phosphorus atoms are affected by the electron-withdrawing group on the phenyl group (**2a**: 56.7, 62.0 ppm, **2h**: 55.7, 60.9 ppm, **2i**: 54.8, 60.1 ppm, **2l**: 56.0, 61.3 ppm, also see Table S1 in Supporting Information), although the substituent and the phosphorus atoms are relatively distant from each other. The X-ray structures of **2c** bearing an electron-donating group and **2i** bearing an electron-withdrawing group revealed that both derivatives also have the same adamantane-like framework (Fig. 1, see Supporting Information).

Table 2
Synthesis of the adamantane-like cage compounds **2**.



Entry	R (**1**)	Obtained Product Yields (%)
1[a]	2'-MeO (**1b**)	**2b**: 14
2[a]	2'-Me (**1c**)	**2c**: 10
3[a]	2'-Br (**1d**)	**2d**: trace
4[a]	2'-NO_2 (**1e**)	N.D.[c]
5[a]	3'-MeO (**1f**)	**2f**: 39

6[a]	3'-Me (**1g**)	**2g**: 46
7[a]	3'-Br (**1h**)	**2h**: 29
8[a]	3'-NO_2 (**1i**)	**2i**: 10
9[b]	4'-MeO (**1j**)	**2j**: 14 + **4j**: 14
10[a]	4'-Me (**1k**)	**2k**: 38
11[b]	4'-Br (**1l**)	**2l**: 32 + **3l**: 16
12[a]	4'-NO_2 (**1m**)	**2m**: trace + **3m**: 6

[a] Purification: short silica gel column with chloroform followed by recrystallization from chloroform.
[b] Purification: recrystallization from chloroform.
[c] N.D. = not detected any adamantane derivatives.

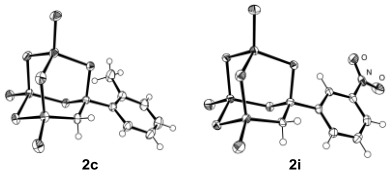
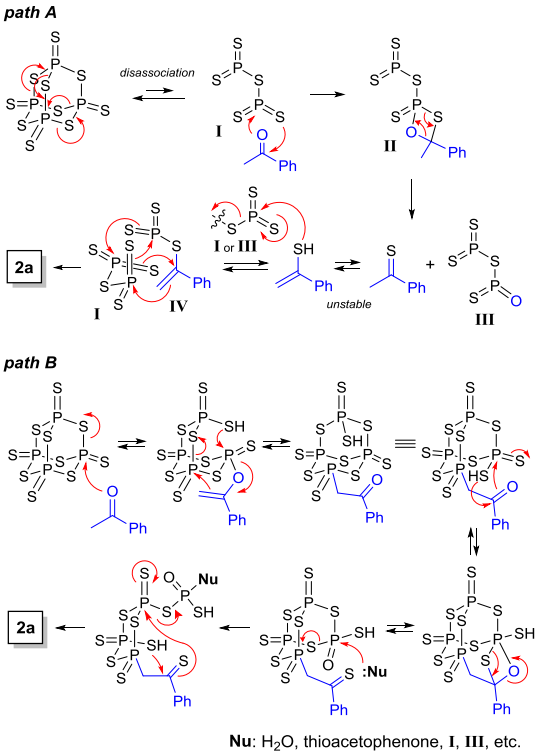


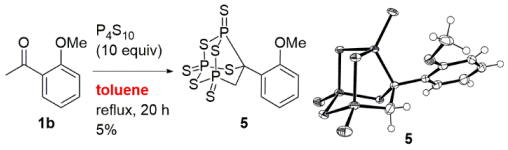
Fig. 1. The X-ray structures of **2c** and **2i**.

The plausible reaction mechanisms for the formation of **2a** are illustrated in Scheme 3, although the reactivity of P_4S_{10} is quite complicated and not yet fully clarified.[3a,11c,17] Path A in Scheme 3 is based on the formation of thioacetophenone *in situ*. In refluxing solvents, P_4S_{10} dissociates into P_2S_5 (**I**) and then, the desired thioacetophenone is formed through forming four-membered ring **II**.[3a,8b,11b,11c,17b,17e,18] Because of the thiocarbonyl group tends to turn into a stable C–S bond,[19] the more reactive enthiol form of thioacetophenone immediately reacts with the fragments **I** or **III** and the generated **IV** recombines with **I** to form **2a**. On the other hand, path B is based on the direct reaction of acetophenone with P_4S_{10}.[20] In this plausible pathway, the temporary thionation of acetophenone occurs in P_4S_{10}-mediated species and the following reassembly of the adamantane-framework gave **2a**.



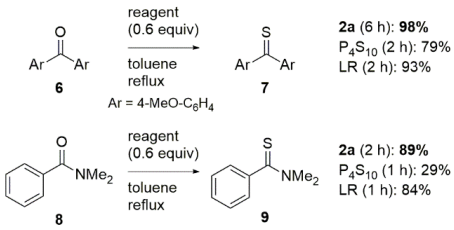
Scheme 3. Possible mechanism for the formation of **2a**.

Surprisingly, we also found that a novel noradamantane-like cage compound **5**, with one sulfur atom removed from **2b**, was formed by the reaction of **1b** with P_4S_{10}, when refluxing toluene was exchanged for benzene as the solvent (Scheme 4). The framework of **5**, consisting of P, S, and C atoms, was determined by X-ray crystallographic analysis (see Supporting Information). To our knowledge, there have been only a few noradamantane skeletons consisting of three elements, such as Si, S, and C atoms,[21] Se, S, and C atoms,[21] C, N, and O atoms,[22] Ge, Si, and S,[23] or Sn, Si, and Se.[23]



Scheme 4. Synthesis of **5** and the X-ray structure of **5**.

The structures of these adamantane-like cage compounds **2** are quite similar to that of P_4S_{10}. Therefore, we also examined the thionation of 4,4'-dimethoxybenzophenone (**6**) and *N*,*N*-dimethylbenzamide (**8**) by using **2a** as a thionating agent, compared with P_4S_{10} and Lawesson's reagent (LR) (Scheme 5). Each reaction was continued until the ketone **6** or the benzamide **8** were completely consumed. As the results of the comparative experiments, the thionating ability of **2a** was superior to those representative agents. One of the most remarkable observations was that **2a** itself had no strong unpleasant smell, which is a significant problem for P_4S_{10} and LR. In addition, these adamantane-like cage compounds **2** dissolved well in benzene or toluene, unlike P_4S_{10}. Therefore, considering the solubility and the substrate-selectivity, **2** might be a good thionating agent.



Scheme 5. Thionation of 4,4'-dimethoxtbenzophenone (**6**) and *N*,*N*-dimethylbenzamide (**8**), using **2a**, P_4S_{10}, or LR.

3. Conclusion

In conclusion, the novel adamantane-like cage compounds **2** and the noradamantane-like cage compound **5**, consisting of the three elements, phosphorus, sulfur, and carbon, were synthesized by the reactions of acetophenone derivatives **1** with P_4S_{10}. These structurally interesting heterogeneous scaffolds and the synthetic method were previously unreported. The first isolations of these compounds **2** and **5** would assist in the full elucidation of the reactivity of P_4S_{10}. In addition, by using **2a**, ketone and benzamide were successfully transformed into the corresponding thioketone and benzothioamide, respectively, in high yields. Therefore, the non-foul smelling, organic soluble **2a** is expected to represent a new-generation of thionating agents. Further physicochemical properties of these cage compounds and the characterization of the intermediates leading to adamantane- or noradamantane-like compounds will be reported in the near future.

4. Experimental section

4.1. General

All melting points were determined on a Yanaco MP melting point (mp) apparatus and are uncorrected. Infrared spectra were recorded with a JASCO FT/IR 4100 spectrophotometer. ^{1}H, ^{13}C, and ^{31}P NMR spectral data were obtained with JEOL JNM-ECS 400 instruments. Chemical shifts are quoted in ppm using tetramethylsilane (δ = 0 ppm) as the reference for ^{1}H NMR spectroscopy, $CDCl_3$ (δ = 77.0 ppm) for ^{13}C NMR spectroscopy, and 85% H_3PO_4 (δ = 0 ppm) for ^{31}P NMR spectroscopy. Mass spectra were measured with a JEOL JMS-T100LP spectrometer. Elemental analysis was performed with a YANACO CHN-CODER JM-10 model analyzer. Column chromatography was carried out on silica gel (spherical, neutral, 40–50 μm, Kanto Chemical Co., Japan).

*4.1.1. General Procedure 1: Synthesis of **2** (recrystallization alone):*

A mixture of acetophenone derivative **1** (0.860 mmol) and P_4S_{10} (8.60 mmol) in benzene (5 mL) was stirred under refluxing temperature for 20 h. After cooling to room temperature, the reaction mixture was filtered through an 11G-4 glass filter and washed with $CHCl_3$ (80 mL). The filtrate was evaporated at 40 °C, and then the residue was purified by recrystallization from hexane/$CHCl_3$ to give **2** as a solid.

*4.1.2. General Procedure 2: Synthesis of **2** (short silica gel column chromatography followed by recrystallization):*

A mixture of acetophenone derivative **1** (2.25 mmol) and P_4S_{10} (22.5 mmol) in benzene (12 mL) was stirred under refluxing temperature for 20 h. After cooling to room temperature, the reaction mixture was filtered through an 11G-4 glass filter and washed with $CHCl_3$ (80 mL). The filtrate was evaporated at 40 °C, and then the residue was filtered through a silica gel column chromatography ($CHCl_3$). The eluate was evaporated at 40 °C, and then the residue was purified by recrystallization from hexane/$CHCl_3$ to give **2** as a solid.

*4.1.3. 7-Phenyl-2,4,6,8,9-pentathia-1,3,5-triphosphaadamantane 1,3,5-trisulfide (**2a**).*

Using Procedure 1; Yield: 46% (179 mg), Colorless crystal; MP 184.2–184.7 °C; IR (KBr): 2920, 2873, 1459, 758, 710, 687, 532 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.14 (d, $^{2}J_{HP}$ = 11.2 Hz, 2H), 7.57–7.61 (m, 3H), 7.62–7.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.8 (d, $^{1}J_{CP}$ = 53.4 Hz), 70.3 (d, $^{2}J_{CP}$ = 8.6 Hz), 125.6, 130.7 (×2), 132.0 (×2), 140.5; ^{31}P NMR (160 MHz, $CDCl_3$) δ 56.7, 62.0; HRMS-ESI (*m*/*z*): $[M + H]^+$ calcd for $C_8H_8P_3S_8$: 452.7605, found: 452.7593; Anal Cacld for $C_8H_7P_3S_8$: C, 21.23; H, 1.56. Found: C, 21.09; H, 1.77.

*4.1.4. 7-(2-Methoxyphenyl)-2,4,6,8,9-pentathia-1,3,5-triphosphaadamantane 1,3,5-trisulfide (**2b**).*

Using Procedure 2; Yield: 14% (146 mg), Colorless crystal; MP 180.2–180.8 °C; IR (KBr): 2935, 2914, 2833, 1459, 756, 687, 532 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.39 (d, $^{2}J_{HP}$ = 10.0 Hz, 2H), 3.94 (s, 3H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.14 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.54 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.5 (d, $^{1}J_{CP}$ = 50.6 Hz), 56.3, 70.1 (d, $^{2}J_{CP}$ = 8.6 Hz), 114.0, 122.0, 126.62, 126.64, 133.0, 157.7; ^{31}P NMR (160 MHz, $CDCl_3$) δ 56.3, 63.1; HRMS-ESI (*m*/*z*): $[M + H]^+$ calcd for $C_9H_{10}OP_3S_8$: 482.7710, found: 482.7699; Anal Cacld for $C_9H_9OP_3S_8$: C, 22.40; H, 1.88. Found: C, 22.66; H, 2.12.

*4.1.5. 7-(o-Tolyl)-2,4,6,8,9-pentathia-1,3,5-triphosphaadamantane 1,3,5-trisulfide (**2c**).*

Using Procedure 2; Yield: 10% (183 mg), Colorless crystal; MP 166.2–166.7 °C; IR (KBr): 2916, 2885, 2861, 1459, 1389, 758, 689, 527 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.68 (s, 3H), 3.21 (d, $^{2}J_{HP}$ = 11.6 Hz, 2H), 7.37–7.51 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.3, 44.2 (d, $^{1}J_{CP}$ = 53.4 Hz), 70.6 (d, $^{2}J_{CP}$ = 9.5 Hz), 125.2, 127.8, 131.4, 135.9, 138.6, The ipso carbon peak was not observed.; ^{31}P NMR (160 MHz, $CDCl_3$) δ 56.6, 60.3; HRMS-ESI (*m*/*z*): $[M + H]^+$ calcd for $C_9H_{10}P_3S_8$: 466.7761, found: 466.7747; Anal Cacld for $C_9H_9P_3S_8$: C, 23.17; H, 1.94. Found: C, 23.02; H, 2.09.

*4.1.6. 7-(3-Methoxyphenyl)-2,4,6,8,9-pentathia-1,3,5-triphosphaadamantane 1,3,5-trisulfide (**2f**).*

Using Procedure 2; Yield: 39% (419 mg), Colorless crystal; MP 181.1–181.7 °C; IR (KBr): 2922, 2869, 2830, 1460, 785, 691, 533 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.12 (d, $^{2}J_{HP}$ = 10.8 Hz, 2H), 3.87 (s, 3H), 7.08 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.14 (dd, *J* = 2.2, 2.2 Hz, 1H), 7.20 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.49 (dd, *J* = 8.2, 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.9 (d, $^{1}J_{CP}$ = 53.4 Hz), 55.9, 111.7, 117.0, 117,1, 131.7, 141.8, 161.2, The quaternary carbon peak was not observed.; ^{31}P NMR (160 MHz, $CDCl_3$) δ 56.7, 62.0; HRMS-ESI (*m*/*z*): $[M + H]^+$ calcd for $C_9H_{10}OP_3S_8$: 482.7710, found: 482.7728; Anal Cacld for $C_9H_9OP_3S_8$: C, 22.40; H, 1.88. Found: C, 22.27; H, 1.99.

*4.1.7. 7-(m-Tolyl)-2,4,6,8,9-pentathia-1,3,5-triphosphaadamantane 1,3,5-trisulfide (**2g**).*

Using Procedure 2; Yield: 46% (480 mg), Colorless crystal; MP 168.6–168.7 °C; IR (KBr): 2915, 2865, 1459, 1389, 780, 692, 533 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.45 (s, 3H), 3.13 (d, $^{2}J_{HP}$ = 10.8 Hz, 2H), 7.36–7.49 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 42.8 (d, $^{1}J_{CP}$ = 54.4 Hz), 122.4, 126.1, 130.5, 132.8, 141.0, The ipso carbon peak and the quaternary carbon peak were not observed.; ^{31}P NMR (160 MHz, $CDCl_3$) δ 56.8, 62.2; HRMS-ESI (*m*/*z*): $[M + H]^+$ calcd for $C_9H_{10}P_3S_8$: 466.7761, found: 466.7762; Anal Cacld for $C_9H_9P_3S_8$: C, 23.17; H, 1.94. Found: C, 23.21; H, 1.98.

*4.1.8. 7-(3-Bromophenyl)-2,4,6,8,9-pentathia-1,3,5-triphosphaadamantane 1,3,5-trisulfide (**2h**).*

Using Procedure 2; Yield: 29% (356 mg), Colorless crystal; MP 181.8–182.5 °C; IR (KBr): 2918, 2871, 1470, 1077, 795, 689, 564, 536 cm-1; 1H NMR (400 MHz, CDCl3) δ 3.10 (d, 2JHP = 10.8 Hz, 2H), 7.47 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.59 (d, *J* = 8.4 Hz, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.76–7.78 (m, 1H); 13C NMR (100 MHz, CDCl3) δ 42.6 (d, 1JCP = 54.4 Hz), 69.5 (d, 2JCP = 7.6 Hz), 124.2, 124.7, 128.7, 132.0, 135.1, 142.4; 31P NMR (160 MHz, CDCl3) δ 55.7, 60.9; HRMS-ESI (*m*/*z*): [M + H]+ calcd for C8H779BrP3S8: 530.6710, found: 530.6731; Anal Cacld for C8H6BrP3S8: C, 18.08; H, 1.14. Found: C, 17.96; H, 1.28.

*4.1.9. 7-(3-Nitrophenyl)-2,4,6,8,9-pentathia-1,3,5-triphosphaadamantane 1,3,5-trisulfide (**2i**).*

Using Procedure 2; Yield: 10% (137 mg), Pale yellow crystal; MP 196.0–196.8 °C; IR (KBr): 2926, 2868, 1523, 1459, 1348, 778, 696, 533 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.18 (d, $^{2}J_{HP}$ = 11.2 Hz, 2H), 7.84 (dd, *J* = 8.0, 8.0 Hz, 1H), 8.03 (dd, *J* = 8.0, 2.0 Hz, 1H), 8.46 (dd, *J* = 8.0, 2.0 Hz, 1H), 8.51 (dd, *J* = 2.0, 2.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.6 (d, $^{1}J_{CP}$ = 54.3 Hz), 69.5 (d, $^{2}J_{CP}$ = 7.6 Hz), 120.9, 126.6, 131.8, 132.0, 142.5, 149.3; ^{31}P NMR (160 MHz, $CDCl_3$) δ 54.8, 60.1; HRMS-ESI (*m*/*z*): $[M + H]^+$ calcd for $C_8H_7NO_2P_3S_8$: 497.7455, found: 497.7478; Anal Cacld for $C_8H_6NO_2P_3S_8$: C, 19.31; H, 1.22; N, 2.81. Found: C, 19.24; H, 1.39; N, 2.89.

*4.1.10. 7-(4-Methoxyphenyl)-2,4,6,8,9-pentathia-1,3,5-triphosphaadamantane 1,3,5-trisulfide (**2j**).*

Using Procedure 1; Yield: 14% (60.0 mg), Colorless crystal; MP 165.7–166.5 °C; IR (KBr): 2918, 2863, 2832, 1459, 684, 530 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.09 (d, $^2J_{HP}$ = 11.0 Hz, 2H), 3.88 (s, 3H), 7.06 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.7 (d, $^1J_{CP}$ = 53.4 Hz), 55.9, 69.9 (ddd, $^2J_{CP}$ = 8.2 Hz, $^2J_{CP}$ = 8.2 Hz, $^2J_{CP}$ = 8.2 Hz), 115.9 (×2), 127.2 (×2), 132.3 (ddd, $^3J_{CP}$ = 21.1 Hz, $^3J_{CP}$ = 8.1 Hz, $^3J_{CP}$ = 8.1 Hz), 162.1; ^{31}P NMR (160 MHz, $CDCl_3$) δ 57.5, 62.6; HRMS-ESI (*m*/*z*): $[M + H]^+$ calcd for $C_9H_{10}OP_3S_8$: 482.7710, found: 482.7723; Anal Cacld for $C_9H_9OP_3S_8$: C, 22.40; H, 1.88. Found: C, 22.15; H, 2.09.

*4.1.11. 7-(p-Tolyl)-2,4,6,8,9-pentathia-1,3,5-triphosphaadamantane 1,3,5-trisulfide (**2k**).*

Using Procedure 2; Yield: 38% (408 mg), Colorless crystal; MP 171.4–171.7 °C; IR (KBr): 2916, 2864, 1459, 1389, 805, 681, 527 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 3.11 (d, $^2J_{HP}$ = 11.0 Hz, 2H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 42.8 (d, $^1J_{CP}$ = 53.4 Hz), 70.1 (d, $^2J_{CP}$ = 8.6 Hz), 125.4 (×2), 131.3 (×2), 137.6, 142.7; ^{31}P NMR (160 MHz, $CDCl_3$) δ 57.1, 62.3; HRMS-ESI (*m*/*z*): $[M + H]^+$ calcd for $C_9H_{10}P_3S_8$: 466.7761, found: 466.7755; Anal Cacld for $C_9H_9P_3S_8$: C, 23.17; H, 1.94. Found: C, 22.97; H, 2.04.

*4.1.12. 7-(4-Bromophenyl)-2,4,6,8,9-pentathia-1,3,5-triphosphaadamantane 1,3,5-trisulfide (**2l**).*

Using Procedure 1; Yield: 32% (99.0 mg), Colorless crystal; MP 205.2–205.6 °C; IR (KBr): 2924, 2876, 1459, 1077, 809, 693, 534, 528 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.09 (d, $^2J_{HP}$ = 11.6 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 7.73 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.6 (d, $^1J_{CP}$ = 54.4 Hz), 69.6–69.9 (m), 126.7, 127.2 (×2), 133.9 (×2), The ipso carbon peak was not observed.; ^{31}P NMR (160 MHz, $CDCl_3$) δ 56.0, 61.3; HRMS-ESI (*m*/*z*): $[M + H]^+$ calcd for $C_8H_7{}^{79}BrP_3S_8$: 530.6710, found: 530.6706; Anal Cacld for $C_8H_6BrP_3S_8$: C, 18.08; H, 1.14. Found: C, 17.91; H, 1.30.

*4.1.13. 7a-(2-Methoxyphenyl)dihydro-2,6-epithio[1,2,5]thiadiphospholo[2,3-d][1,3,2,4]dithiadiphosphole 2,4,6-trisulfide (**5**).*

Using Procedure 1; Yield: 5% (76.2 mg), Colorless crystal; MP 213.9–214.4 °C; IR (KBr): 2929, 2912, 2826, 1459, 750, 692, 528 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 3.38 (ddd, $^2J_{HP}$ = 39.6 Hz, 14.4 Hz, $^3J_{HP}$ = 10.4 Hz, 1H), 3.87 (s, 3H), 4.46 (dd, *J* = 14.4 Hz, $^2J_{HP}$ = 12.0 Hz, 1H), 7.03 (d, *J* = 8.0 Hz, 1H), 7.09 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.35–7.40 (m, 1H), 7.49–7.54 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 55.2 (dd, $^1J_{CP}$ = 50.3 Hz, $^2J_{CP}$ = 11.4 Hz), 55.6, 113.0 (d, *J* = 2.9 Hz), 119.9–120.0 (m), 121.8 (d, *J* = 2.0 Hz), 126.9 (d, *J* = 6.7 Hz), 132.7 (d, *J* = 3.8 Hz), 156.7 (d, *J* = 4.7 Hz), The quaternary carbon peak was not observed; ^{31}P NMR (160 MHz, $CDCl_3$) δ 55.0, 69.8, 124.1; HRMS-ESI (*m*/*z*): $[M + H]^+$ calcd for $C_9H_{10}OP_3S_7$: 450.7989, found: 450.7992; Anal Cacld for $C_9H_9OP_3S_7$: C, 23.99; H, 2.01. Found: C, 23.83; H, 2.09.

*4.1.14. Synthesis of **7**. (Scheme 5):*

A mixture of **6** (25.0 mg, 0.105 mmol) and P_4S_{10} (29.0 mg, 0.0630 mmol) in toluene (2 mL) was stirred under refluxing temperature for 6 h. After the evaporation of the solvent, the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 30/1) to give **7**[24] as a dark blue solid (26.6 mg, 98%).

*4.1.15. Synthesis of **9**. (Scheme 5):*

A mixture of **8** (28.0 mg, 0.188 mmol) and P_4S_{10} (51.0 mg, 0.113 mmol) in toluene (2 mL) was stirred under refluxing temperature for 2 h. After the evaporation of the solvent, the residue was purified by silica gel column chromatography (hexane/ethyl acetate = 10/1) to give **9**[25] as a pale yellow solid (27.8 mg, 89%).

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